

SUBSTITUTED DERIVATIVES OF
TUNGSTEN HEXAFLUORIDE

by

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of the requirements for the degree of Doctor of Philosophy.

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This thesis describes the original work of the author, except where specific references are given to the work of others. The present work was carried out in the Chemistry Department of the University of Glasgow between November 1969 and June 1972.

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ABSTRACT

This thesis describes the preparations of series of derivatives of tungsten (VI) fluorides, and experimental techniques, used to investigate their physical and chemical properties, particularly ^{19}F n.m.r spectroscopy and ^{18}F tracer techniques.

The substituents X of the series $\text{WF}_{6-n}\text{X}_n$ which are investigated are $-\text{NMe}_2$, $-\text{NEt}_2$, $-\text{OC}_6\text{F}_5$, $-\text{OC}(\text{O})\text{R}$ (where $\text{R}=\text{Me}$ or CF_3), CN , NCO and Cl . They were chosen to develop different aspects of the chemistry of W(VI) , in particular to investigate the effects of ligands of different electronic and steric properties on the reactivities and stereochemistry of the compounds.

Dialkylamino derivatives of tungsten hexafluoride of the type $\text{WF}_{6-n}(\text{NR}_2)_n$ ($\text{R}=\text{Me}$, $n=1$; $\text{R}=\text{Et}$, $n=1, 2$ and 4) are obtained from the stoichiometric reactions of tungsten hexafluoride with dialkylamino trimethylsilanes. Attempts to prepare $\text{WF}_3(\text{NEt}_2)_3$ by this method were unsuccessful and led to the formation of $\text{WF}_4(\text{NEt}_2)_2$ or a mixture of unidentified species. The physical properties of WF_5NR_2 and $\text{WF}_4(\text{NEt}_2)_2$ are consistent with their being associated but $\text{WF}_2(\text{NEt}_2)_4$ appears to be monomeric. Substitution of the fluoride by chloride, rather than W-N bond cleavage, occurs in reactions of WF_5NEt_2 with anhydrous hydrogen chloride. Analyses of the compounds obtained from the reactions of WF_5NEt_2 with Me_3SiCl are consistent with the presence of more than one species, which are not completely characterized. WF_5NEt_2 reacts with $(\text{MeO})_2\text{S}=\text{O}$ giving $\text{WF}_4(\text{NEt}_2)\{\text{OS}(\text{O})\text{OMe}\}$ which slowly decomposes to $\text{WF}_4(\text{OMe})(\text{NEt}_2)$. The N.m.r spectra of the products from the reactions of WF_5NEt_2 with trimethylmethoxysilane are consistent with the presence of more than one species. $\text{WF}(\text{OMe})_2(\text{NEt}_2)_3$ and $\text{WCl}_2(\text{NEt}_2)_3$ are obtained from the reactions of $\text{WF}_2(\text{NEt}_2)_4$ with Me_3SiOMe and Me_3SiCl respectively.

The reactions of tungsten hexafluoride with tris (dimethylamino) phosphine and trimethylsilyl imidazole are also described. Tungsten hexafluoride undergoes aminolysis with diethylamine, which has been followed by conductometric titrations in acetone solution.

$\text{WF}_5\text{OC}_6\text{F}_5$ and $\text{MoF}_5\text{OC}_6\text{F}_5$ are prepared from the reaction of WF_6 with $\text{Me}_3\text{SiOC}_6\text{F}_5$ (1:1 mole ratio). The molecular weight determinations and ^{19}F n.m.r spectrum of $\text{WF}_5\text{OC}_6\text{F}_5$ are consistent with its monomeric nature. The difference in the ortho and para fluorine chemical shifts of pentafluorophenyl group in $\text{WF}_5\text{OC}_6\text{F}_5$ is smallest among the pentafluorophenyl derivatives, which suggests that $-\text{OWF}_5$ is an π electron acceptor group. The colour of both $\text{WF}_5\text{OC}_6\text{F}_5$ and $\text{MoF}_5\text{OC}_6\text{F}_5$ is ascribed to intramolecular charge transfer from the pentafluorophenyl ring to the non bonding orbitals of tungsten. The ^{19}F n.m.r spectrum of the product obtained from the reaction of WF_6 (1 mole) with $\text{Me}_3\text{SiOC}_6\text{F}_5$ (2 moles) is consistent with a mixture including $\text{WF}_5\text{OC}_6\text{F}_5$ and $\text{WF}_4(\text{OC}_6\text{F}_5)_2$.

Carboxylato tungsten (VI) fluorides cannot be isolated from the reactions of WF_6 with $\text{Me}_3\text{SiOC}(\text{O})\text{R}$, where $\text{R}=\text{CH}_3, \text{CF}_3, \text{C}_3\text{F}_7$. Tungsten hexafluoride undergoes substitution reaction with Me_3SiX ($\text{X}=\text{CN}$ or NCO), but the products are not completely characterized.

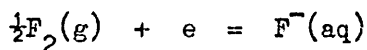
A fluorine - 18 tracer technique has been developed to study the exchange reactions of $\text{WF}_{6-n}\text{X}_n$ (where $\text{X}=\text{NEt}_2, \text{OMe}, \text{OPh}, \text{OC}_6\text{F}_5; n=1-4$) with Me_3SiF . The rate of exchange depends on the nature and number of substituents, concentrations, stoichiometry of the reactants and the reaction conditions. The mechanism of the exchange reactions can be related to the mechanism of substitution reactions.

INTRODUCTION

Knowledge of the chemistry and technology of fluorine and its compounds has expanded enormously in recent years. Since 1940, when research into both organic and inorganic compounds of fluorine was stimulated by their importance in the development of nuclear science, fluorine compounds have been increasingly used as refrigerants, plastics, elastomers, surfactants, and high energy rocket fuels. At the same time the chemistry of fluorine has been shown to encompass some of the most inert and the most reactive classes of compounds, namely the fluorocarbons and halogen fluorides, and therefore presents a number of challenging problems on the nature of the chemical bonding, structure, and reactivity.

Being the most reactive member of the periodic table, fluorine combines with most of the elements, even with some of the noble gases. Its reactivity is attributed to the low bond dissociation energy of the fluorine molecule. The most recent determination, by photo-ionization methods¹ gives a value of $36.67 \pm 0.23 \text{ kcal.mol}^{-1}$, compared with the latest values for the dissociation energies of other halogens,^{2,3} of Cl_2 , 57.2; Br_2 , 45.4; and I_2 , 35.6 kcal.mol^{-1} . The large inter-electronic repulsion forces of the fluorine molecule and the absence of orbitals of suitable symmetry for multiple bonding have been suggested as the possible causes of the weakness of the F-F bond.

Fluorine is the most electronegative of the elements and its high ionization potential precludes the possibility of positive oxidation states. Fluorine compounds with the elements are of two main types, ionic and covalent, in both of which the fluorine has a complete octet of electrons. The stability of the fluoride ion is reflected in the estimated standard electrode potential for the system



of $E^0 = +2.85$ v. The co-ordination number of fluorine in covalent fluorides is usually one, but an increasing number of compounds are being shown to contain bridging fluorine atoms (e.g. refs. 4,5). It is also currently suggested that the filled 2p orbitals of fluorine can engage in π -bonding where suitable orbitals exist in the heteroatom (e.g. refs. 6,7).

The small size of the fluorine atom is responsible for the highest covalency of the element with which it combines, and also accounts for many inorganic fluorides having physical and chemical properties different from those of the corresponding chlorides, bromides and iodides.

Fluorine-19 is the only naturally occurring isotope of the element. This nucleus, with a spin of $\frac{1}{2}$, has a gyromagnetic ratio very near to that of protium, and hence ^{19}F nuclear magnetic resonance spectra are easily measured. Since the range of ^{19}F chemical shifts and coupling constants is large compared with that obtained from 1H n.m.r. spectra, much useful information about molecular structures may be obtained from n.m.r. spectral data. In this study of some fluorine compounds of tungsten, a great use of ^{19}F n.m.r. spectroscopy has been made in the characterization of the reaction products.

Fluorine has a number of radioactive nuclides of which fluorine-18 has the longest half life (112 minutes).⁸ This half life is relatively short in comparison with other nuclides used as radio-active tracers, and effectively limits the period over which tracer experiments may be carried out. This has been a serious limitation on its use, since it cannot be stored, but must be prepared each day and used at the site of preparation. With the increasing number of nuclear reactors and high energy accelerators such as cyclotrons and betatrons the availability of

^{18}F in mechanistic studies can provide a means of investigating chemical bonding, from which a knowledge of the strength and nature of bonds in a molecule can be obtained. ^{18}F Tracer studies have been extensively used to investigate the nature of metal-ligand interactions and the mechanisms of various reactions studied during the course of this work.

Among the known binary fluorides, the hexafluorides form an interesting, and in some respects an unusual class of compounds. Hexafluorides are known for the group VI elements, sulphur, selenium, tellurium and polonium, xenon, chromium and some of the second and third row transition and actinide metals. In general, the non-metal hexafluorides are considered to be less reactive than the metal hexafluorides. In fact very little attention has been paid to the chemical reactivities of transition metal fluorides, compared with the non-metal fluorides. Early studies were restricted in the main to the measurement of physical properties, and even in the case of the technologically important uranium hexafluoride very little investigation was made of its chemical properties and reactions prior to 1957.^{9,10} Still less was known about other higher transition metal fluorides. Clark¹¹ reported in 1958 that most of the hexafluorides had only been studied qualitatively and the reaction products had not been identified. They were assumed to be extremely reactive, however, for the only property common to all of them appeared to be their ability to undergo violent hydrolysis reactions.

Over the last decade, the discovery of suitable material such as the polymers "Teflon" and "Kel-F" and the development of experimental techniques have enabled the metal hexafluorides to be handled under anhydrous conditions. A number of excellent reviews are available which

deal with the preparation and properties of transition metal fluorides. Emeleus¹² and Peacock¹³ have summed up the earlier developments, while more recent progress has been covered briefly by Simons,¹⁴ Weinstock,¹⁵ Bartlett,^{7,17} Fergusson,¹⁷ Canterford, Colten, and O'Donnell.^{6,9}

The hexafluorides of second and third row transition metals are monomeric and volatile at room temperature. They are characterized by extremely short liquid ranges. Absence of strong intermolecular forces, between electronegative fluorine atoms is believed to be the main reason for this unexpected high volatility of these fluorides. Hexafluorides of the third transition series are more volatile than the corresponding second row hexafluorides, this phenomenon cannot be explained in terms of the conventional concept of an inverse relationship between molecular weight and volatility. It has been suggested that, entropy considerations are important at elevated temperatures owing to the intermolecular forces being almost identical on the periphery of the molecules.¹⁸ Tungsten hexafluoride, a colourless liquid is the most volatile of the transition metal hexafluorides, m.p. 2.0° , b.p. 17.1° (ref. 19) and this property allows it to be handled by conventional vacuum line techniques.

The hexafluorides form regular octahedral molecules, as has been demonstrated by infra-red and Raman,⁶ ^{19}F n.m.r. spectroscopy²⁰ and electron diffraction.^{21,22} Force constants for the symmetric metal-fluorine stretching vibrations of gaseous transition metal hexafluorides have been recently calculated.²³ The highest value is found for WF_6 , which suggests that it is the most stable and therefore the least reactive chemically. The enthalpies of formation of molybdenum and tungsten hexafluorides have been determined by fluorine bomb calorimetry,^{24,25} and average bond energies of 107 and 121 kcal.mol⁻¹

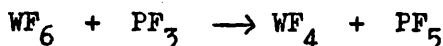
respectively can be derived.⁷ These values are much higher than those of sulphur, selenium and tellurium hexafluorides which are 79, 73 and 81 kcal.mol⁻¹ respectively.^{7,26}

The available comparative studies of the chemical reactivities of the transition metal hexafluorides confirm the above predictions. Tungsten hexafluoride is the least reactive, and has been used as a solvent for n.m.r. studies of other fluorides.²⁷ Platinum hexafluoride on the other hand, is extremely reactive. It can oxidise molecular oxygen,²⁸ xenon,²⁹ and bromine trifluoride to bromine pentafluoride.³⁰ From a study of the reactions of the hexafluorides of the third transition series with nitric oxide and nitrosyl fluoride, Bartlett and co-workers^{7,31} concluded that the electron affinities are in the order $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$. They observed, however, that the ability of the hexafluorides to accept fluoride ion to give MF_7^- and MF_8^{2-} species decreases along this series, and they attributed the effect to a sharp increase in ligand crowding from WF_6 to PtF_6 .

In order to account for the trends in the stability and reactivity of the metal hexafluorides, it has been suggested that there is fluorine-to-metal π -bonding, and that the contribution of π -bonding to the total bonding decreases as the number of electrons in the metal t_{2g} orbitals increases, resulting in decreasing stability and consequently increasing reactivity from left to right across the series.^{6,7} It is expected that π -bonding will be greater in the hexafluorides of the third transition series than in those of the second transition series because of the greater nuclear charges of the central atoms of the former. Bartlett⁷ has suggested that the constancy of the M-F bond lengths in the third row hexafluorides^{21,22} may result from a coincidental matching of the lengthening due to loss of multiple bond

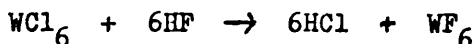
character with a shortening from the transition series contraction.

Molybdenum and tungsten hexafluorides were long regarded as very reactive compounds, and very similar in physical and chemical properties.³² The assumption that their chemical properties are very similar appears to have been based on the similarity of their hydrolysis reactions. Recent work, however, indicates that there are considerable differences in chemical reactivity. O'Donnell and Stewart³³ have studied oxidation reduction and halogen exchange reactions of the higher fluorides of chromium, molybdenum, and tungsten with lower fluorides of some non-metals and some non-metal chlorides, and have found that the order of reactivity is $\text{CrF}_5 > \text{MoF}_6 > \text{WF}_6$. MoF_6 is a weak fluorinating agent towards PF_3 , CS_2 and WF_4 , giving PF_5 , $(\text{CF}_3)_2\text{S}_2$ and WF_6 respectively, the other product in each case being MoF_5 . Halogen exchange occurs between MoF_6 and PCl_3 , AsCl_3 , SbCl_3 , TiCl_4 , CCl_4 , SiCl_4 , BCl_3 and PBr_3 . WF_6 is virtually inert as a fluorinating agent, only reacting slowly with PF_3 :



WF_6 undergoes halogen-exchange reactions with TiCl_4 and BCl_3 to give WCl_6 and WCl_3F_3 respectively. A slow reaction also occurs between WF_6 and PBr_3 yielding WBr_5 and PF_3 . The reactions of the hexafluorides of molybdenum, tungsten and uranium with binary ionic chlorides have been studied by O'Donnell and Wilson,³⁴ and these provide further evidence of the relatively inert nature of WF_6 compared with MoF_6 and UF_6 . Halogen exchange was observed between WF_6 and BeCl_2 to yield WCl_6 and BeF_2 .

Tungsten hexafluoride was prepared by Ruff and co-workers in 1905 by the reaction



and they carried out the first qualitative investigation of its chemical behaviour.^{35,36} Direct fluorination of the metal is now the preferred method of preparation,^{37,38} but despite the work done on its preparation, purification and physical characteristics, in common with the other metal hexafluorides, few investigations of its chemistry have been made.

The first quantitative investigation of tungsten hexafluoride was undertaken by Clark and Emeléus.³⁹ The adducts $WF_6 \cdot 4.5SO_3$, $WF_6 \cdot (NH_3)_4$, $WF_6 \cdot (Py)_3$, and $WF_6 (CH_3NH_2)_3$ were reported, but none of these was well characterized. 1:1 Adducts of WF_6 with pyridine, PMe_3 and NR_3 and a 1:2 adduct with pyridine were later reported by Muettterties.⁴⁰ N.m.r. spectroscopic equivalence of fluorine atoms has been observed from these complexes.⁴¹ It is proposed that spectroscopic equivalence in these complexes results from intramolecular exchange. 1:2 Complexes of WF_6 with Et_2S and Et_2Se have recently been isolated.⁴² The ^{19}F nuclear magnetic resonance spectra of both these complexes are similar to those of other WF_6 , donor complexes. Reaction of Me_2O , Et_2O and $Me_3SiOSiMe_3$ with WF_6 led to the preparation of WOF_4OMe_2 , WOF_4OEt_2 and WOF_4 respectively.^{42,43} The formation of these complexes demonstrates the great stability of a multiple W-O bond.

Charge transfer interactions have been observed between WF_6 and the group IV compounds, MX_4 ($M = Si, Ge, Sn, X = \text{alkyl}; M = C, Si, Sn; X = Cl$), C_6H_6 , $C_6H_5CH_3$, C_6F_6 , n-hexane and cyclo-hexane.⁴⁴⁻⁴⁷ Charge transfer from solvent to the transition metal fluoride is suggested to be the dominant electronic transition observed in these solutions, but the possibility of the fluoride also behaving as a donor to non-bonding orbitals localised on Si, Ge or Sn cannot be

excluded. Photolysis of solutions of WF_6 in C_6H_6 , $C_6H_5CH_3$ and $(CH_3)_4Sn$ leads to reduction of W(VI), but no discrete compounds are isolated. Tungsten tetrafluoride, which, has been previously made⁴⁴ from the reaction of WF_6 with C_6H_6 at 110° , was not observed in the photolysis of WF_6 solutions in benzene.⁴⁷

Following the preparation of WF_5Cl ,^{33,48,49} interest in the substituted derivatives of tungsten hexafluoride has increased. Other members of the series $WF_{6-n}Cl_n$ ($n = 1-5$) have been characterized.⁵⁰ A mixture of cis and trans WCl_2F_4 isolated from the controlled fluorination of WCl_6 with fluorine, decomposes readily to give other members of the series, $WF_{6-n}Cl_n$, and these compounds were observed by n.m.r. spectroscopy during the reaction of WF_6 with Me_3SiCl .⁵⁰ ^{19}F N.m.r., vibrational, and microwave spectra are all consistent with a monomeric structure for these compounds.⁵⁰⁻⁵²

Series of methoxy tungsten(VI) fluorides and phenoxy tungsten(VI) fluorides $WF_{6-n}(OR)_n$ ($R = Me$; $n = 1-4$; $R = Ph$; $n = 1$ or 2) have been reported from the reactions of tungsten hexafluoride with $R_{4-n}Si(OR)_n$.^{43,53} A very recent report described the preparation of the corresponding methoxy compounds of tungsten hexachloride, and it is suggested that the two series are interconvertible through fluorination of W-Cl bonds with SbF_3 or chlorination of W-F bonds with Me_3SiCl .⁵⁴ Substitution beyond $n = 4$ is not affected with Me_3SiOMe but can be achieved with CH_3O^- to give the $(MeO)_5WCl$ and $(MeO)_5W$ species.⁵⁴ N.m.r. studies indicate that, like the chlorofluorides, these species are monomeric in solution and in some cases geometric isomers are present. Whereas $(CH_3O)_2WF_4$ and $(C_6H_5O)_2WF_4$ compounds exists exclusively in the cis configuration trans-tetramethoxytungstendichloride has been isolated from the selective chlorination of the difluoride.⁵⁴

Binary fluorides have been widely used as fluorinating agents, particularly in organic chemistry (e.g. sulphur tetrafluoride).⁵⁵ Tungsten hexafluoride has been described both as a powerful fluorinating agent³² and as having no fluorinating action.⁵⁶ Both of these conclusions, however, are based on few experimental observations.

The work outlined above leads to the conclusion that tungsten hexafluoride is the least reactive of the transition metal hexafluorides, and is less readily reduced than molybdenum hexafluoride or uranium hexafluoride. The formation of tungsten chlorofluorides and methoxy and phenoxy fluorides suggests, that it is a mild, selective, fluorinating agent with limited application.

The work described in this thesis was undertaken with the intention of extending the chemistry of tungsten hexafluoride by preparing some of its derivatives, particularly dialkylamino compounds, in order to investigate their physical and chemical properties. The study of the compounds, of stoichiometry WF_4XX' , $WF_3XX'X''$, $WF_2XX',X''X'''$ etc. where XX' etc. are different ligands such as NR_2 , OR, Cl, was undertaken with the aim of getting structural information, particularly about the ligands' electronic and steric factors that determine the stereochemistry of substituted transition metal fluorides. Comparison of the ease of formation and chemical reactivities of various substituted derivatives of tungsten hexafluoride may also lead to useful information regarding the nature of metal-ligand interactions involving a metal in a high oxidation state.

CHAPTER ONE

NITROGEN-TUNGSTEN-FLUORINE COMPOUNDS. THE REACTIONS OF
TUNGSTEN HEXAFLUORIDE WITH SOME ORGANOSILICON COMPOUNDS.
THE PREPARATION AND REACTIONS OF DIALKYLAMINO DERIVATIVES
OF TUNGSTEN HEXAFLUORIDE.

INTRODUCTION

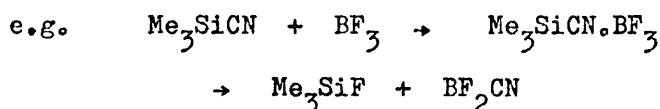
Interest in the substituted derivatives of transition metal fluorides has in the past been mainly limited to those containing chloro and alkoxy (or aryloxy) substituents, while potential nitrogen donors have been ignored. The only dialkylamino derivatives of transition metal fluorides reported when this work was started, were the dialkylamino titanium(IV) trifluorides, TiF_3NR_2 , which have been isolated from the reactions of TiF_4 with secondary amines.^{57,58}

Previous efforts to prepare the derivatives of transition metal halides have generally involved treating the metal chlorides or oxychlorides either with protic ligands, for example ROH ⁵⁹ or RNH_2 ,⁶⁰ where R = alkyl or aryl, or with salts such as $RONa$, R_2NLi or C_5H_5Na .^{61,62} Even for an individual element there is no obvious trend in these reactions, since although substitution reactions may result in such products as $(Me_2N)_6W$ ⁶¹ and $(Me_3SiCH_2)_6W$,⁶³ other procedures produce reduced oligomeric products, for example $(EtO)_6W_2Cl_4$,⁶⁴ and $[(C_6F_5)_3W(OEt_2)_3]$,⁵⁴ Cleavage reactions of SiX bond (X = OR or NR_2 etc.) in Me_3SiX by non-metal fluorides have provided a versatile method for the synthesis of substituted derivatives by means of the general reaction⁶⁵:



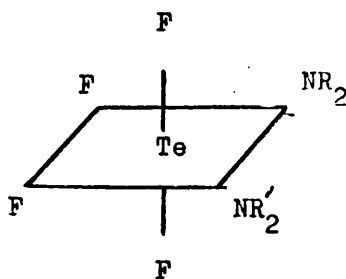
Where R is an alkyl group and M the transition metal. These reactions

are thought to proceed through an intermediate Lewis acid, Lewis base complex, which can in some cases be isolated.⁶⁶



The complex may dissociate before substitution occurs resulting in no apparent reaction. The cleavage of a Si-X bond in Me_3SiX ($\text{X} = \text{Cl}$, OMe or OPh) by tungsten hexafluoride to yield a series of substituted tungsten(VI) fluorides $\text{WF}_{6-n}\text{X}_n$ and Me_3SiF has been reported,^{43,48-50,53,54} and in the present work it was hoped that the interaction of tungsten hexafluoride with NN-dialkyltrimethylsilylamine would provide a route to hitherto unreported dialkylamino derivatives of WF_6 . The reactions of tungsten hexafluoride and molybdenum hexafluoride with dialkylamino-trimethylsilane have been briefly investigated.^{87,105}

A recent report has described the preparation of various dialkylamino tellurium(VI) fluorides from the reaction of TeF_6 with Me_3SiNR_2 ($\text{R} = \text{Et}$ or Me)⁶⁷ but, although one fluorine atom in the tellurium hexafluoride molecule can be substituted readily by a dialkylamino group giving TeF_5NMe_2 and TeF_5Net_2 respectively, only the dimethylamino ligand formed a stable bis-substituted product. The mixed dimethylamino diethylamino-tellurium tetrafluoride, $\text{TeF}_4(\text{Net}_2\text{NMe}_2)$ was so unstable that it could only be characterized by its ^{19}F n.m.r. spectrum. The ^{19}F n.m.r. spectrum of both $\text{TeF}_4(\text{NMe}_2)_2$ and $\text{TeF}_4(\text{NMe}_2)(\text{Net}_2)$ have been interpreted in terms of a cis structure (I).



(I)

Dialkylamino compounds of the type $\text{MF}_{5-n}(\text{NEt}_2)_n$ [$\text{M} = \text{Nb}$ or Ta ; $n = 1$ or 2] have been recently isolated from the reactions of MF_5 or MF_5OEt_2 with $\text{Me}_3\text{SiNEt}_2$.⁶⁸ From their vibrational spectra these compounds appear to be polymeric with bridging fluorine atoms, and like the pentafluorides and $(\text{MF}_{5-n}\text{Cl}_n)_n$ compounds they form complexes with pyridine and substituted pyridine bases.

There has been growing interest in the use of substituted phosphines, especially aminophosphines, as ligands towards transition metal, metal and non-metal compounds.^{69,70} Thionyl fluoride undergoes substitution with tris(dimethylamino)phosphine giving $\text{Me}_2\text{NS(O)F}$, and sulphur tetrafluoride oxidises phosphine to P(V) thus giving $(\text{Me}_2\text{N})_3\text{PF}_2$ and $(\text{Me}_2\text{N})_2\text{PF}_3$. The sulphur species from these reactions could not be identified.⁷¹ Tungsten hexafluoride, being a very weak oxidising agent, is expected to undergo substitution reactions with tris(dimethylamino)phosphine.

The present reactions were undertaken to prepare tungsten fluorine compounds with nitrogen substituents in order to make comparisons with other substituted transition metal fluorides containing metal-oxygen and metal-chlorine bonds. Detailed study of the chemical reactivity of dialkylamino tungsten(VI) fluorides was carried out for two purposes. The first was to compare the Lewis acid character of dialkylamino tungsten(VI) fluorides with that of tungsten hexafluoride itself. The second was to prepare derivatives of tungsten hexafluoride such as $\text{WF}_4\text{XX}'$, $\text{WF}_3\text{XXX}''$ etc. where X , X' etc are NR_2 , Cl , OR etc. Such derivatives were required to investigate how the stereochemistry of substituted transition metal fluorides is determined by the ligands' steric and electronic requirements.

Covalent transition metal halides undergo solvolysis, for example, when they react with liquid ammonia,⁷² or with primary or secondary amines.⁷³

For a particular halide the degree of solvolysis decreases along the series NH_3 , NH_2R , NHR_2 and the products become increasingly soluble in organic solvents. Simple adducts are normally formed initially between halides and tertiary amines although prolonged interaction often results in reduction of the metal to a lower valency state.⁷⁴ Tungsten(VI) chloride reacts with liquid ammonia to give the ammoniates $\text{WCl}_6 \cdot 4\text{NH}_3$ and $\text{WCl}_6 \cdot 6\text{NH}_3$, but these subsequently undergo ammonolysis with the formation of $\text{WCl}_5 \cdot (\text{NH}_2)$ and $\text{WCl}_4(\text{NH}_2)_2$ respectively.⁷² Aminobasic tungsten(VI) chlorides, $\text{WCl}_2(\text{NHR})_4$ ($\text{R} = \text{Pr}^n$ or Bu^n) have been isolated from the reactions of WCl_6 with propylamine and butylamine, and analogous compounds are believed to be present in the products formed with methylamine and ethylamine. With secondary amines initial co-ordination of the amine is followed by reduction, giving the W(IV) complex salts, $(\text{NH}_2\text{R}_2)_2(\text{WCl}_6)$, aminolysis then produces the compounds $\text{WCl}_3(\text{NR}_2)_2 \cdot 2\text{NHR}_2$. On the basis of elemental analysis tertiary amines also appear to give the adducts $\text{WCl}_6 \cdot \text{NR}_3$ initially but subsequent reaction again leads to the production of tungsten(IV) complexes, $(\text{NHR}_3)_2(\text{WCl}_6)$.⁶⁰ Similar aminolysis reactions have been described for Nb, Ta, Mo and Ti halides of the type MX_5 .^{72,73,75,76}

Few aminolysis reactions of transition metal fluorides have been reported. Titanium tetrafluoride undergoes aminolysis with primary and secondary amines yielding TiF_3NR_2 and $[\text{R}_2\text{NH}_2]_2[\text{TiF}_6^{2-}]$.^{57,58} Recent attempts to isolate the reported⁷⁷ adducts $\text{NbF}_5 \cdot (\text{NHEt}_2)_2$ and $\text{TaF}_5(\text{Et}_2\text{NH})_2$ led to aminolysis. Further investigation may show other fluorides undergo aminolysis.⁷⁸

Tungsten hexafluoride has been reported to form 1:3 and 1:1 complexes with primary and tertiary amines respectively,^{39,40} but no aminolysis products were noted in these reactions. The behaviour of tungsten hexafluoride with secondary amines was investigated as it might be expected to be intermediate between that of the primary and tertiary amine reactions.

RESULTS AND DISCUSSION

INTERACTION OF DIALKYLAMINO TRIMETHYLSILANES WITH TUNGSTEN HEXAFLUORIDE.

Formation of Dialkylamino Tungsten(VI) Fluorides

Dialkylamino trimethylsilanes react exothermically with tungsten hexafluoride below 20° to give trimethylfluorosilane and viscous, dark red brown liquids or solids, which are involatile at 20° and are readily hydrolysed by water or alkali. These involatile products are formulated on the basis of elemental analysis and spectroscopic properties as $WF_{6-n}(NR_2)_n$ ($R = Me, n = 1$; $R = Et, n = 1, 2$ and 4). The reactions of dimethylaminotrimethylsilane with tungsten hexafluoride are less satisfactory than the reactions of diethylaminotrimethylsilane, as the characterization of the products from the former reactions is more difficult than for the products of the latter reactions.

Reaction of dimethylaminotrimethylsilane with excess tungsten hexafluoride gives dimethylaminotungsten(VI) pentafluoride, WF_5NMe_2 , which is a dark red viscous liquid. It is decomposed by MeCN, $MeNO_2$ and acetone, and is insoluble in most of the other organic solvents. Reproducible analytical, density and viscosity data (see Table 1.4 and page 45) for WF_5NMe_2 are consistent with the presence of a pure compound. Its infra-red spectrum contains bands in the region $1155-955\text{ cm}^{-1}$ characteristic of a $-NMe_2$ group,⁸⁶ but the occurrence of strong bands in the region $700-600\text{ cm}^{-1}$, due to W-F stretching modes, makes the assignment of the W-N stretching mode difficult. Due to its insolubility no n.m.r. studies could be performed on this compound.

Insufficient evidence is available to claim the isolation of bis(dimethylamino)tungsten(VI) tetrafluoride, $WF_4(NMe_2)_2$. Reaction of tungsten hexafluoride with two-fold excess of dimethylaminotrimethylsilane led to the formation of a dark red viscous liquid resembling WF_5NMe_2 . The analysis of this liquid is not consistent with the presence of a pure compound.

Lack of a suitable solvent and the relatively higher viscosity of dimethylaminotungsten(VI) fluorides compared with the corresponding diethylamino compounds made their detailed study very difficult. Owing to such difficulties, the isolation of the higher members of the series $WF_{6-n}(NMe_2)_n$ was not attempted. There is no reason, however, that such compounds should not exist, particularly since the highest member of the series i.e. $W(NMe_2)_6$ is known.⁶¹

The reaction of diethylaminotrimethylsilane with tungsten hexafluoride is different from the corresponding reaction of TeF_6 with Me_3SiNEt_2 . Whereas substitution beyond one fluorine atom was not achieved in the latter case,⁶⁷ up to four fluorine atoms could be replaced in the former case. Moreover the tellurium compounds are monomeric in solution, whereas the diethylaminotungsten(VI) fluorides appear to be associated.

Products obtained from the reaction of WF_6 with Me_3SiNEt_2 generally correspond to the stoichiometry of the reactants used. Diethylaminotungsten(VI) pentafluoride, WF_5NEt_2 and bis(diethylamino)tungsten(VI) tetrafluoride, $WF_4(NEt_2)_2$, are dark red viscous liquids which are slightly soluble in C_6F_6 and toluene. The tetrakis(diethylamino)tungsten(VI) difluoride, $WF_2(NEt_2)_4$, on the other hand is a dark red solid which is freely soluble in C_6F_6 and CS_2 . These compounds are all decomposed by CH_3CN , CH_3NO_2 and acetone. Tris(diethylamino)tungsten(VI) trifluoride, $WF_3(NEt_2)_3$ could not be isolated. Reactions designed to prepare this compound led to the formation of either $WF_4(NEt_2)_2$ or products which, from

their analysis appeared to be mixtures. These could neither be separated, nor characterized. This is surprising, particularly when the corresponding methoxy and chloro compounds $[WCl_3F_3, WF_3(OMe)_3]$ are well characterized.^{43,50}

Under the experimental conditions used, substitution beyond the fourth fluorine atom was not achieved, but there is no obvious reason why the last two fluorines should not be substituted, particularly as $WF(OMe)_5$, $W(OMe)_6$, $WFCl_5$, $W(OC_6H_5)_6$, $W(OC_6F_5)_6$, $W(NMe_2)_6$ and the very recently reported $W(CH_3)_6$ are known.^{49,54,59,61,89,90}

PROPERTIES OF DIALKYLAMINOTUNGSTEN(VI) FLUORIDES

The densities of WF_6 ⁷⁹ and dialkylaminotungsten(VI) fluorides are in the order :

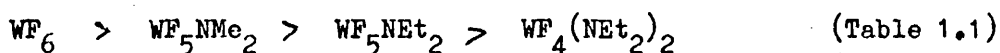


Table 1.1

Compound	Density ($g\text{ cm}^{-3}$)
WF_6	3.44
WF_5NMe_2	2.82
WF_5NEt_2	2.37
$WF_4(NEt_2)_2$	2.10

Since an increase in mass of the ligand X ($X = F, NMe_2, NEt_2$) should cause a decrease in the density of the compound, the observed order of densities is not unexpected. However, the rate of decrease of densities is not linear and the difference in the densities of WF_6 and dialkylaminotungsten(VI) fluorides seems to be too big to be accounted for

on the basis of mass effects only. Some other factors appear likely to be involved in these density changes. One such factor could be the association in these molecules. In the associated state molecules are expected to be less dense than in the monomeric state. Having assumed that these compounds are associated, the relative difference in the densities of these compounds can be used to discuss the degree of association in dialkylaminotungsten(VI) fluorides. The difference between the densities of $WF_4(NEt_2)_2$ and $WF_5(NEt_2)$ is small compared with the difference between WF_5NMe_2 and WF_5NEt_2 and the difference between WF_6 and the dialkylaminotungsten(VI) fluorides. This suggests a smaller degree of polymerization in $WF_4(NEt_2)_2$ than in WF_5NR_2 . In general the degree of polymerization would be expected to decrease with the increase in substitution of $-NR_2$ ligands in WF_6 . In fact $WF_2(NEt_2)_4$ appears to be monomeric on the basis of molecular weight determinations (Found, 360; $WF_2(NEt_2)_4$ requires, 310). However, due to the lack of molecular weight results for other dialkylaminotungsten(VI) fluorides, it is unsatisfactory to say anything conclusively about the degree of association in these compounds.

Dialkylamino derivatives of titanium tetra halides and 1:1 amine complexes of various metal fluorides (e.g. Ti, Zr, Si, Ge, Sn, S, Te, Mo) have been found to be associated.^{57,58,81,82} Moreover, it has been suggested that association in various metal dialkylamides of the type $M(NR_2)_n$ ($M = Ti, Mo; n = 4; M = Nb, Ta; n = 5$) is prevented by steric interactions, and the degree of association in $Zr(NR_2)_4$ is reported to be 1.22.^{84,85}

By analogy, association in the lower members of dialkylaminotungsten(VI) fluorides and the monomeric nature of higher dialkylaminotungsten(VI)

fluoride is not unlikely. The insolubility and high viscosity of WF_5NR_2 ($R = Me$ or Et) and $WF_4(NEt_2)_2$ also favours association in these molecules. On the other hand absence of polymerization in $WF_2(NEt_2)_4$ as a result of the steric repulsions of $-NEt_2$ groups, is supported by the related complexes of $W(NMe_2)_6$,⁶¹ and $WCl_2(NHR)_4$,⁶⁰ which are known to be monomers.

Having assumed that WF_5NEt_2 , WF_5NMe_2 and $WF_4(NEt_2)_2$ are associated, the question remains whether such association is through fluorine bridges or dialkylamino groups? The absence of polymerization in chlorotungsten(VI) fluorides and alkoxy and phenoxy tungsten(VI) fluoride favours the likelihood of association through the dialkylamino groups. On the other hand the dialkylamino group is the least electronegative in the series $F > Cl > OMe > OPh > NR_2$ and inductive effects will tend to delocalise the charge towards the fluorine atoms of the dialkylaminotungsten(VI) fluorides. This would both strengthen the W-N bonds and enhance the ability of fluorine to take part in intermolecular bonding. Moreover, fluorine bridges are very common in metal fluorides and their complexes, for example 1:1 amine complexes of metal fluorides mentioned above are believed to be fluorine bridged, and niobium pentafluoride and tantalum pentafluorides^{5,83} are also known to be associated through fluorine bridges. It seems, therefore, more probable to assume that association between the molecules of dialkylaminotungsten(VI) fluorides is through fluorine rather than dialkylamino bridges.

The infra-red spectra of the dialkylaminotungsten(VI) fluorides in the region $4000-400\text{ cm}^{-1}$ are remarkably similar. A broad band of variable intensity at about 3200 cm^{-1} with a shoulder at 3130 cm^{-1} was observed in all cases, in addition to the three bands (two in the case of WF_5NMe_2 at 3035 and 2930 cm^{-1}) in the region $2995-2880\text{ cm}^{-1}$ characteristic of

$\nu(\text{C-H})$ vibrations. These absorptions may be due to a species containing a N-H group,^{85a} but such an impurity must be present in very small concentrations in view of the reproducible, analytical density and viscosity data obtained.

The presence of a strong band at 1720 cm^{-1} with a shoulder at 1700 cm^{-1} in WF_5NMe_2 and a weak band at 1685 cm^{-1} with shoulder at 1708 cm^{-1} in WF_5Net_2 is not understood. These bands are not present in the infra-red spectra of other diethylaminotungsten(VI) fluorides.

Assignments in the $1200\text{--}400\text{ cm}^{-1}$ region are given in Table 1.2. Bands in the region $1000\text{--}1200\text{ cm}^{-1}$ are assigned to diethylamino groups on the basis of Bradley's work on metal dialkylamides and by comparison with the corresponding assignments made for dialkylaminotellurium(VI) fluorides.⁶⁷ Assignments in the region $800\text{--}400\text{ cm}^{-1}$ are very difficult, as absorptions such as $\nu(\text{W-F})$, $\nu(\text{W-N})$ and bridging fluorine are expected in this region.^{51,67,85a,86,86a} However it seems reasonable to assign the bands in the region $(800\text{--}640)\text{cm}^{-1}$ to the $\nu(\text{W-F})$ stretching vibrations by comparison with the chlorotungsten(VI) fluorides and other related compounds for example SF_5Cl ^{87a} and dialkylaminotellurium(VI) fluorides.⁶⁷ It is not possible however, to distinguish between $\nu(\text{W-N})$ and bridging $\nu(\text{W-F})$ vibrations in the region $(650\text{--}400\text{ cm}^{-1})$.

The molecular structure of $\text{W}(\text{NMe}_2)_6$ suggests that $\text{W} \leftarrow \text{N } d^{\pi} \leftarrow p^{\pi}$ bonding is important and a similar conclusion has been reached from the infra-red spectra of other transition metal dialkylamides.⁸⁶ By analogy it seems reasonable to expect $\text{N} \rightarrow \text{W } p^{\pi} \rightarrow d^{\pi}$ bonding in dialkylaminotungsten(VI) fluorides, but due to the difficulty of unambiguous assignments for tungsten-nitrogen stretching modes, it is hard to draw any definite conclusions.

The ^1H n.m.r. spectra (Table 1.3) of WF_5Net_2 , $\text{WF}_4(\text{Net}_2)_2$ and $\text{WF}_2(\text{Net}_2)_4$

Table 1.2

The vibrational frequencies (cm^{-1}) and the assignments for diethylaminotungsten(VI) fluorides.

WF_5Net_2	$\text{WF}_4(\text{Net}_2)_2$	$\text{WF}_2(\text{Net}_2)_4$	Assignments
1185 m	1190 m	1185 s	NC_2 asym.
1159 w	1141 m	1145 w	or
1124 m	1130 w	1130 s	CH_3 rocking
1089 s	1090 m	1090 s	
1064 s	1065 m	1065 s	
1020 s	1012 m	1020 sh	sym. NC_2
1000 sh	992 s	1002 s	
910 sh	908 m		
895 m	895 m	895 s	?
855 w			
797 s	795 m	800 s	
779 sh			
695 s	661 m	695 s	Discussed in
(585-650)br,s	640 m		the text.
	600s	600 br,s	
	555 w		
	508 w		
465 w	460 w	465 m,br	
		420 sh	

br = broad; s = strong; m = medium; w = weak; sh = shoulder

Table 1.3

N.m.r. Chemical Shifts

Compound	¹ H Chemical Shifts ^a			¹⁹ F Chemical Shifts ^b
	(p.p.m.)			(p.p.m.)
	δ -CCH ₃	δ WNCH ₂	?	
WF ₅ Net ₂	1.1(t) ^c	5.7(q) ^{c'}	6.7(s)	-128 ± 2(s)
WF ₄ (Net ₂) ₂	1.3(t?)	4.2(br)	6.3(s)	-
WF ₂ (Net ₂) ₄	1.26(t?)	4.3(br)	-	+20.9(s); +16.0(s)
WF ₅ Net ₂ (Heated to 200° in vacuum)	1.13(c)	5.6(c)	3.0(c)	-33.0(c), -61.4(c) -141.6(s)

a = low field of Me₄Si; b = negative value low field of CCl₃F and positive value up field of CCl₃F; c' = J(CH₃-CH₂) = 7 Hz.; c = complex; br = broad; t = triplet; (t?) = poorly resolved, appears to be a triplet; q = quartet; s = singlet

are consistent with the presence of -Net_2 groups. The sharp singlet often observed at ca. 6.7 p.p.m. could be due either to slight hydrolysis or to some W=NR species produced in secondary reactions. But the sharpness of the signal makes the second possibility unlikely.

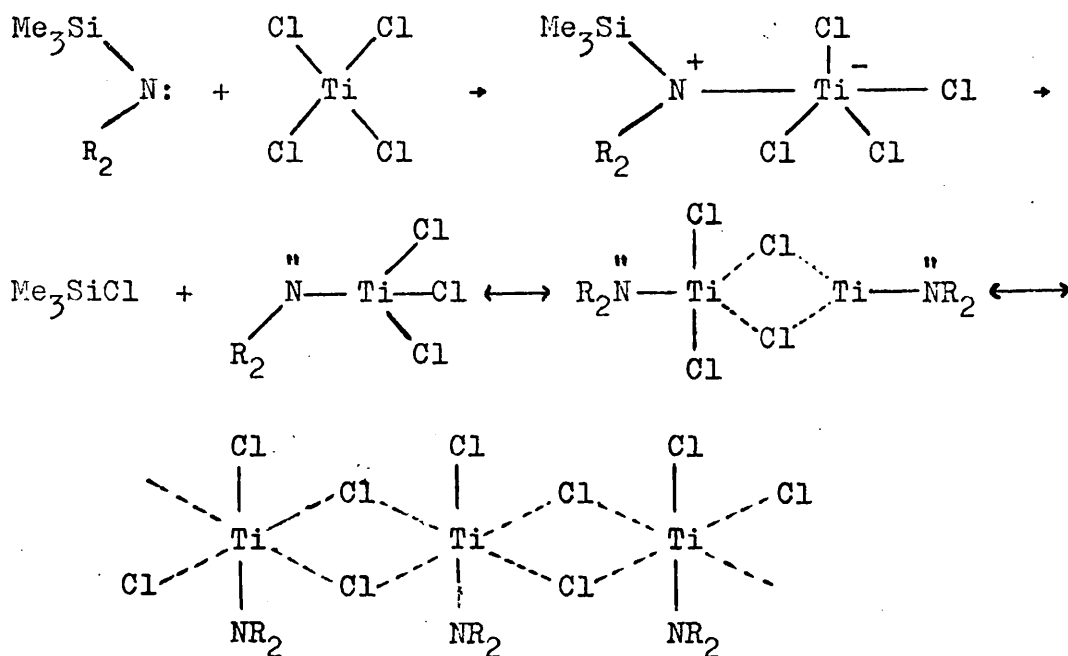
The ^{19}F n.m.r. spectra of WF_5Net_2 and $\text{WF}_2(\text{Net}_2)_4$ were always single broad peaks which is consistent with the occurrence of fast ^{19}F exchange processes. On one occasion the singlet due to WF_5Net_2 was resolved to a doublet at -50° , but the quintet could not be observed. Since WF_5Net_2 appears to be associated, this anomalous result is not understood. Reproducible ^{19}F n.m.r. spectra for $\text{WF}_4(\text{Net}_2)_2$ could not be obtained. The ^{19}F n.m.r. spectrum of $\text{WF}_2(\text{Net}_2)_4$ consists of two signals (both single lines) at +21.0 and 16.0 p.p.m. On one occasion only the signal at 21 p.p.m. was observed. The signal at +21 p.p.m. was always the most intense. The relative intensities were different for different samples but in most cases approximate relative intensities were 3:1. Although the assignments of the single line n.m.r. signals are never satisfactory it seems likely that the signals at +21 and +16 p.p.m. could be due to cis and trans $\text{WF}_2(\text{Net}_2)_4$ respectively. However, the broadness of the ^1H signal for $\text{WF}_2(\text{Net}_2)_4$ makes tentative assignments difficult.

Some decomposition of WF_5Net_2 , with the loss of ethylene and ethyl flouride, occurs above 100°C but the ^1H n.m.r. chemical shifts of samples previously heated to 200°C in vacuo show that some W-Net_2 groups are still present. The infra-red spectrum of the above product is also consistent with the presence of -Net_2 group (band in the region $1160\text{-}1015\text{ cm}^{-1}$). The thermal decomposition behaviour of WF_5Net_2 is different from that of WF_5Cl and WF_5OR ($\text{R} = \text{Me}$ or Et). Decomposition of WF_5Cl proceeds with the rearrangement to other members of the series $\text{WF}_n\text{Cl}_{6-n}$ ($n = 0\text{-}6$), and WF_5OR decomposes to give WOF_4 and RF .^{48,87} Moreover, the latter compounds

decompose at a much lower temperature (20°C) compared with WF_5NEt_2 which decomposes slowly above 100°C . Since these compounds have different structures, their ease of decomposition cannot be used as a guide for the comparison of the W-N bond stability in dialkylaminotungsten(VI) fluorides with the W-Cl and W-O bond stabilities in the chlorotungsten(VI) fluorides and alkoxytungsten(VI) fluorides respectively.

Mechanisms of the reactions of Dialkylaminotrimethylsilanes with Tungsten Hexafluoride.

Bürger et al.⁸¹ have described the reaction of diethylamino-trimethylsilane with TiCl_4 as an $\text{S}_{\text{N}}2$ type. They suggested the following reaction scheme leading to the polymeric diethylamino Ti(IV) chlorides.



The reaction of WF_6 with Me_3SiCl has also been discussed in terms of an $\text{S}_{\text{N}}2$ displacement at tungsten by Me_3SiCl .⁵⁰ By analogy it is reasonable to assume that a similar kind of mechanism is involved in the reactions of WF_6 with Me_3SiNR_2 . Undoubtedly an important factor in this type of reaction would be the formation of a very strong Si-F bond. In comparison

with the Si-N bond energy, ($77.0 \text{ Kcal.mol}^{-1}$) the Si-F bond energy is high, ($135.0 \text{ Kcal.mol}^{-1}$). Together with the good acceptor properties of W(VI) fluorides this probably accounts for the ease with which replacement of a fluoride ligand is achieved.

The mechanism of these reactions is further discussed in Chapter 3 in connection with ^{18}F tracer studies.

REACTIONS OF DIETHYLAMINO TUNGSTEN(VI) FLUORIDES

Reaction of Dimethyl Sulphite with Diethylaminotungsten(VI)pentafluoride

Diethylaminotungsten(VI)pentafluoride and dimethyl sulphite react smoothly at 20° to give sulphur dioxide, methyl fluoride and a dark brown viscous liquid. Analyses of different samples of the liquid, prepared under similar experimental conditions, are not reproducible, varying between the extremes, $\text{WF}_4(\text{OMe})(\text{Net}_2)$ and $\text{WF}_4(\text{Net}_2)[\text{OS}(\text{O})\text{OMe}]$.

In one of the reactions of dimethyl sulphite with WF_5Net_2 , methyl fluoride and a dark brown viscous liquid was obtained. The brown liquid involatile at 20° is formulated, on the basis of analytical and spectroscopic evidence, as $\text{WF}_4(\text{Net}_2)[\text{OS}(\text{O})\text{OMe}]$. It is soluble in C_6F_6 , giving a brown solution, and decomposes slowly above 20°C but rapidly at 100° to give sulphur dioxide and methyl fluoride.

The ^1H n.m.r. spectrum of $\text{WF}_4(\text{Net}_2)[\text{OS}(\text{O})\text{OMe}]$ (I) consists of three broad signals at 5.4, 3.1 and 1.3 p.p.m., and a sharp singlet at 3.6 p.p.m. The signals at 1.3 and 5.4 p.p.m. are characteristic of an $-\text{Net}_2$ group, by comparison with WF_5Net_2 (Table 1.3). The intense single line signal at 3.6 p.p.m. is assigned to $-\text{SOCH}_3$, by analogy with the chemical shift of $(\text{MeO})_2\text{S}=\text{O}$ (3.6 p.p.m.). The signal at 3.1 p.p.m. is the least intense. It seems reasonable to assign this signal to small amounts of $\text{WF}_4(\text{Net}_2)(\text{OMe})^{80}$ produced from the slight decomposition of $\text{WF}_4\text{Net}_2.[\text{OS}(\text{O})\text{OMe}]$. The ^{19}F n.m.r. spectrum of product (I) consists of a weak signal at -59.8 p.p.m. which appears to be a doublet. Due to its low intensity it is difficult to make any assignment for this signal.

The infra-red spectrum of product (I) contains a strong band at 1210 cm^{-1} . By comparison with the $(\text{S}=\text{O})$ stretching modes of $(\text{RO})_2\text{SO}$ and $\text{ROS}(\text{O})\text{F}$ ($\text{R} = \text{Me}$ or Et), at 1208 cm^{-1} and 1260 cm^{-1} respectively,^{91a} it seems reasonable to assign this band to an $(\text{S}=\text{O})$ absorption. Some doubt

remains, however, because the characteristic absorption of the -Net_2 group occurs close to this region. The bands in the region $1069\text{--}960\text{ cm}^{-1}$ are assigned to the -Net_2 group by comparison with other metal dialkylamides.⁸⁶ $\nu(\text{W-F})$ and $\nu(\text{W-N})$ absorptions occur in the region $(800\text{--}455)\text{cm}^{-1}$ of the spectrum.

A second reaction of dimethyl sulphite with WF_5Net_2 led to the formation of sulphur dioxide, methyl fluoride and a brown viscous liquid which was slightly soluble in C_6F_6 . The brown liquid involatile at 20° , is formulated from its analysis as $\text{WF}_4(\text{Net}_2)(\text{OMe})$. Its ^1H n.m.r. spectrum contains a sharp singlet at 3.5 p.p.m. characteristic of -SOCH_3 ⁸⁰ in addition to the signal for an -Net_2 group, at 1.2 and 5.2 p.p.m., and a WOMe group at 2.9 p.p.m. This signal (at 3.5 p.p.m.) is thought to be due to some undecomposed $\text{WF}_4(\text{Net}_2)[\text{OS}(\text{O})\text{OMe}]$ or small amount of $(\text{MeO})_2\text{S=O}$ complexed with $\text{WF}_4(\text{Net}_2)(\text{OMe})$. The ^{19}F n.m.r. spectrum of $\text{WF}_4(\text{Net}_2)(\text{OMe})$ consists of three poorly resolved, weak multiplets at -61.3, -51.0 and 34.9 p.p.m. Since the signals are very weak and not clearly resolved, any assignments must be unreliable.

The infra-red spectrum of $\text{WF}_4(\text{Net}_2)(\text{OMe})$ contains strong and medium bands in the region $(1190\text{--}995)\text{cm}^{-1}$ characteristic of an -Net_2 group.⁸⁶ The strong band at 1210 cm^{-1} , assigned to $\nu(\text{S=O})$ in $\text{WF}_4(\text{Net}_2)[\text{OS}(\text{O})\text{OMe}]$, is not observed for $\text{WF}_4(\text{Net}_2)(\text{OMe})$. This implies the absence of any (S=O) containing species in the latter compound, which is consistent with its analysis. The spectrum in the $(900\text{--}460)\text{cm}^{-1}$ region is similar to product (I).

Products from other reactions appear to be mixtures on the basis of the following observations. These reactions proceed with the formation of SO_2 , MeF and dark brown viscous liquids involatile at 20° . This behaviour is similar to reaction (2), and thus one of the products expected

from these reactions is $\text{WF}_4(\text{NEt}_2)(\text{OMe})$. However, these products decompose giving SO_2 and MeF and thus resemble the products of reaction (I). On some occasions $(\text{MeO})_2\text{S}$ was also evolved from the thermal decomposition. The analyses and n.m.r. spectra of these compounds correspond to mixtures of $\text{WF}_4(\text{OMe})(\text{NEt}_2)$ (II) and $\text{WF}_4(\text{NEt}_2)[\text{OS}(\text{O})\text{OMe}]$ (I). Their infra-red spectra are similar to that of product (I).

From the evidence so far presented, it seems reasonable to assume that $\text{WF}_4(\text{NEt}_2)[\text{OS}(\text{O})\text{OMe}]$ is the initial product of the reaction of WF_6 with $(\text{MeO})_2\text{S}=\text{O}$ but it decomposes slowly to $\text{WF}_4(\text{NEt}_2)(\text{OMe})$ and SO_2 . The evolution of $(\text{MeO})_2\text{S}=\text{O}$ from the thermal decomposition of some samples of these compounds can be accounted for by considering that these compounds are weakly complexed by $(\text{MeO})_2\text{S}=\text{O}$.

Reactions of Diethylaminotungsten(VI)pentafluoride with Dimethyldimethoxysilane and with Trimethylmethoxysilane.

Dimethyldimethoxysilane and trimethylmethoxysilane react with diethylaminotungsten(VI)pentafluoride at 20° to give Me_2SiF_2 or Me_3SiF and dark red viscous liquids or solids, which are involatile at 20°C . The involatile products are slightly soluble in C_6F_6 giving light brown solutions, and are readily hydrolysed by H_2O or aqueous alkali. On the basis of analyses, products from the reactions of WF_5NEt_2 with dimethyldimethoxysilane, $\text{Me}_2\text{Si}(\text{OMe})_2$ are formulated as $\text{WF}_4(\text{NEt}_2)(\text{OMe})$ and $\text{WF}_2(\text{NEt}_2)(\text{OMe})_3$. The analyses of the compounds obtained from the reactions of trimethylmethoxysilane, Me_3SiOMe , with WF_5NEt_2 correspond to $\text{WF}_4(\text{NEt}_2)(\text{OMe})$ and $\text{WF}_3(\text{NEt}_2)(\text{OMe})_2$.

The ^1H n.m.r. spectra of these compounds are very complicated and suggest that more than one species is present. The spectra contain a

series of signals in the range 2.8 to 4.4 p.p.m. in addition to the signals characteristic of an -NEt_2 group⁸⁰ at 1.0 ± 0.2 and 5.0 ± 0.4 p.p.m. No ^{19}F n.m.r. signals are observed for the product formulated as $\text{WF}_2(\text{NEt}_2)(\text{OMe})_3$. Spectra of the other compounds described above contain a common singlet at $+17 \pm 1$ p.p.m., in addition to a singlet at $+42.3$ p.p.m. observed for $\text{WF}_3(\text{NEt}_2)(\text{OMe})_2$ only. Due to the possibility of geometrical isomerism and the absence of fine structure in the ^{19}F n.m.r. spectra, assignments for the n.m.r. signals are difficult.

The infra-red spectra of the compounds described above contain a series of bands in the region $(1190-960)\text{cm}^{-1}$. These bands are assigned to -NEt_2 groups by comparison with diethylaminotungsten(VI)fluorides and other related compounds.^{86,85a} Bands in the region $(800-450)\text{cm}^{-1}$ are assigned to $\nu(\text{W-F})$, $\nu(\text{W-N})$ and $\nu(\text{W-O})$.^{67,85a,86}

The mechanism of the reactions of WF_5NEt_2 with dimethyldimethoxysilane and trimethylmethoxysilane is not clear. Presumably the reactions are similar to the corresponding reactions of tungsten hexafluoride with excess trimethylchlorosilane or trimethylmethoxysilane where a mixture of various species is obtained.^{50,87} The two reactions are different, however, in that, whereas satisfactory characterization of the various species obtained in the latter cases is possible from n.m.r. spectroscopy, the viscous nature and insolubility of the dialkylaminomethoxytungsten(VI)fluorides preclude good n.m.r. studies and hence the complete characterization of these products.

Reactions of Diethylaminotungsten(VI)pentafluoride with Anhydrous Hydrogen Chloride or Trimethylchlorosilane.

Reaction of anhydrous hydrogen chloride, HCl with WF_5NEt_2 was expected to proceed with the W-N bond cleaved:



However, no evidence for such a reaction could be obtained. Analysis and infra-red spectra of the products obtained from these reactions are consistent with the substitution of fluoride in WF_5NEt_2 by chloride. The use of trimethylchlorosilane, for substituting fluoride in WF_5NEt_2 , was found to be more convenient than anhydrous hydrogen chloride for the following reasons. Complications arising from the production of HF in the reactions of HCl with WF_5NEt_2 do not arise in the reactions of WF_5NEt_2 with Me_3SiCl . It is safer to work with large quantities of Me_3SiCl than with HCl. Drastic conditions, for example heating or shaking, can be applied in the Me_3SiCl reactions, but not in the HCl reactions. Since Me_3SiCl is a volatile liquid, it is easily handled under vacuum, and reactions in the liquid phase are expected to proceed more smoothly than liquid-gas phase reactions. Finally, the reaction of tungsten hexafluoride with trimethylchlorosilane has been well studied and offers comparative data.

The reaction of WF_5NEt_2 with Me_3SiCl is slow at 20° and heating to 100° or shaking at 20° is necessary to increase the rate of reaction. The products are Me_3SiF , and black sticky solids involatile at 20° . These solids are insoluble in most of the common organic solvents, for example C_6F_6 , CS_2 , CHCl_3 , CCl_4 , Me_4Si , CCl_3F , benzene, toluene and hexane. They are more resistant to hydrolysis by water or aqueous alkali than other dialkylamino tungsten(VI) fluorides. Small quantities of an orange solid are often observed in the products of these reactions but separation by solvent extraction, using the above mentioned solvents, could not be effected.

The analytical results, though they correspond to a mixture of compounds in most cases, suggest that substitution by chloride of four

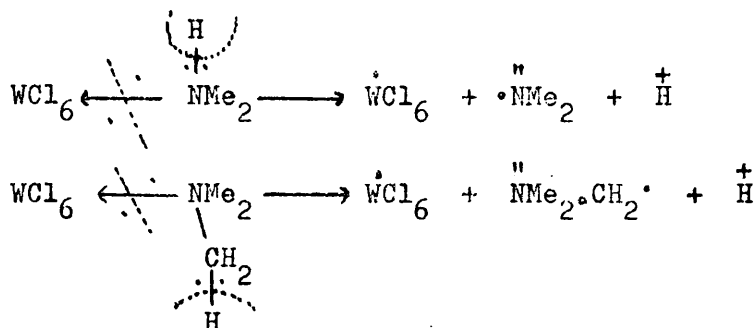
fluorides in WF_5NEt_2 proceeds without reduction of tungsten(VI).

Substitution of the last fluoride of WF_5NEt_2 , however, appears to result in a solid which analyses as $\text{WCl}_4(\text{NEt}_2)$.

The infra-red spectra of these compounds contain weak or medium strong bands in the region $1000\text{--}1200\text{ cm}^{-1}$ characteristic of the --NEt_2 group.⁸⁶ The presence of strong bands at 789 cm^{-1} and 755 cm^{-1} even in $\text{WCl}_4(\text{NEt}_2)$ suggests that a W-F species is still present in the final products. In the $(700\text{--}500)\text{cm}^{-1}$ region both $\nu(\text{W--N})$ and $\nu(\text{W--F})$ modes are expected so no definite assignments can be made. By analogy with the chlorotungsten(VI)fluorides,⁵¹ the (W--Cl) stretching frequency is expected below 400 cm^{-1} but no absorption is observed in this region.

No n.m.r. results are available for the chloro dialkylamino tungsten(VI) fluorides, since a suitable solvent was not found.

Oxidation titrations did not give satisfactory results. The oxidation number of W was found to be 3.7, by reacting $\text{WCl}_4(\text{NEt}_2)$ with excess of standard potassium permanganate solution, and titrating unreacted KMnO_4 solution with sodium oxalate solution. It is presumed that the ambiguity of the results is due to some oxidation of chloride ions to chlorine in these reactions and better results may have been obtained by titrating with potassium dichromate solutions.^{91b} However, reduction of W(VI) to W(V) in these reactions seems likely in the light of the reported reductions of W(VI) in the aminolysis reactions of tungsten hexachloride by tertiary or secondary amines.⁶⁰ It was proposed that, "Co-ordination of a molecule of secondary or tertiary amine to W(VI) is followed by the transfer of an electron from nitrogen to tungsten, and the elimination of a proton by the splitting of an N-H (for secondary amines) or C-H (for tertiary amines) bond.

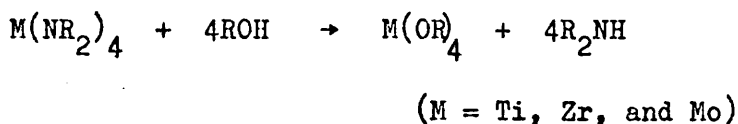


The radical formed could dimerise or react further with the solvent or excess of amine."⁶⁰

The mechanism of reduction in the present case is not clear, but it is likely that $\text{WCl}_5(\text{NEt}_2)$ or a seven co-ordinate intermediate $[\text{WCl}_4 \cdot (\text{NEt}_2)\text{Me}_3\text{SiCl}]$ is reduced according to some similar reaction scheme.

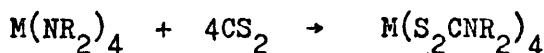
Behaviour of Carbon Disulphide and Methanol towards Tetrakis(diethyl-amino)tungsten(VI)difluoride and Diethylaminotungsten(VI)pentafluoride.

Alcohols were reported to react with metal dialkylamides producing metal alkoxides according to the reaction.⁸⁴



The reverse reaction did not occur even under forcing conditions which implies that M-O bonds are stronger than M-N bonds.

Carbon disulphide reacts quantitatively with metal dialkylamides giving N,N,dialkyldithiocarbamates.⁸⁵



The behaviour of methanol and carbon disulphide towards WF_5NEt_2 and $\text{WF}_2(\text{NEt}_2)_4$ differs from its behaviour with metal dialkylamides described above. CS_2 does not react with WF_5NEt_2 at 20° even after shaking.

$\text{WF}_2(\text{Net}_2)_4$ is soluble in CS_2 , without chemical reaction, as indicated by the n.m.r. spectrum of the solution, (Table 1.4). The WF_5Net_2 reaction with methanol is similar to its reactions with CH_3NO_2 and CH_3CN in which decomposition occurs. $\text{WF}_2(\text{Net}_2)_4$ appears to react very slowly with methanol, (see n.m.r. Table 1.4) but the products cannot be identified.

Table 1.4

N.m.r. spectra of $\text{WF}_2(\text{Net}_2)_4$ in various solvents.

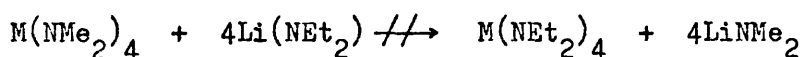
Solvent	^1H Chemical Shifts (p.p.m.)			^{19}F Chemical Shifts (p.p.m.)
	$-\text{CCH}_3$	WNCH_2		
C_6F_6	1.26(t)	4.3 br	-	+17.0(s), +21.4(s)
CS_2	1.26(t)	4.7 br	-	+16.5(s), +21.1(s)
$\text{CS}_2 + \text{C}_6\text{F}_6$	1.26(t)	4.7 br	-	+20.9(s)
MeOH	1.37(t)	4.5 br	3.3(s), 5.8? (MeOH)	+20.3(s)
				+49.8(s), +129.2(s)
				(?) (?)

The different behaviour of diethylaminotungsten(VI)fluorides towards CS_2 and MeOH suggests a greater stability of W-N bonds in these compounds compared with the metal dialkylamides of Ti, Zr, Ta and Mo.^{84,85,86.}

Reactions of Tetrakis(diethylamino)tungsten(VI)difluoride with
Trimethylchlorosilane or Trimethylmethoxysilane

$\text{WF}_2(\text{Net}_2)_4$ reacts smoothly at 20° with Me_3SiCl and Me_3SiOMe . The rate increases on shaking the reaction vessel. Whereas the W-N bond

could not be broken in WF_5NET_2 . One $-\text{NET}_2$ group is replaced by Cl or OMe in these reactions of $\text{WF}_2(\text{NET}_2)_4$, which suggests significant steric interactions in this compound. This is not unlikely and is in line with the reactions of metal dialkylamides,⁸⁴ where the substitution of dimethylamino group, by LiNMe_2 , in place of diethylamino group occurs readily. In contrast, substitution of the diethylamino group by $\text{Li}(\text{NET}_2)$ in metal dimethylamides could not be achieved.



(M = Ti, Zr, Mo)

The products from the reactions of $\text{WF}_2(\text{NET}_2)_4$ with Me_3SiCl and Me_3SiOMe are red brown solids, soluble in C_6F_6 . These are formulated as $\text{WFCl}_2(\text{NET}_2)_3$ and $\text{WF}(\text{OMe})_2(\text{NET}_2)_3$ on the basis of their elemental analyses.

The ^1H n.m.r. spectrum of $\text{WF}(\text{OMe})_2(\text{NET}_2)_3$ contains signals assigned to $-\text{NET}_2$ group⁸⁰ at 1.1 ± 0.5 and 4.35 ± 0.15 p.p.m. in addition to a signal at 3.3 p.p.m. (single line). By comparison with the ^1H n.m.r. spectrum of $\text{WF}_4(\text{NET}_2)_2(\text{OMe})_2$,⁸⁰ the latter signal is assigned to (W-OMe) group. The ^1H n.m.r. spectrum of $\text{WFCl}_2(\text{NET}_2)_3$ consists of only two broad signals at 0.9 and 4.6 p.p.m., assigned to the $-\text{NET}_2$ group by comparison with the chemical shifts of $\text{WF}_2(\text{NET}_2)_4$ (Table 1.3).

Considerable difficulty was experienced in obtaining ^{19}F n.m.r. signals for $\text{WF}(\text{OMe})_2(\text{NET}_2)_3$ and $\text{WFCl}_2(\text{NET}_2)_3$. ^{19}F n.m.r. spectra could only be obtained for one sample in each case.

The ^{19}F n.m.r. spectrum of $\text{WFCl}_2(\text{NET}_2)_3$ consists of a major signal (single line) at -46.7 p.p.m., in addition to a minor signal (single line, very weak in intensity) at +15.0 p.p.m. The latter signal is assigned to

unreacted $\text{WF}_2(\text{Net}_2)_4$ by comparison with the ^{19}F n.m.r. chemical shifts of $\text{WF}_2(\text{Net}_2)_4$, (Table 1.3). The ^{19}F n.m.r. spectrum of $\text{WF}(\text{OMe})_2(\text{Net}_2)_3$ contains only one singlet at +63.7 p.p.m. which may be compared with the chemical shift of $\text{WF}(\text{OMe})_5$ (39.5 p.p.m.).⁸⁷

The infra-red spectra of both $\text{WFCl}_2(\text{Net}_2)_3$ and $\text{WF}(\text{OMe})_2(\text{Net}_2)_3$ are very similar in the $-\text{Net}_2$ region (1000-1200) cm^{-1} . The bands at 799 and 772 cm^{-1} in the spectrum of $\text{WFCl}_2(\text{Net}_2)_3$ and at 790 cm^{-1} for $\text{WF}(\text{OMe})_2(\text{Net}_2)_3$ are assigned to W-F stretching vibrations.^{51,67} Assignments for $\nu(\text{W-N})$ and $\nu(\text{W-O})$ [latter in $\text{WF}(\text{OMe})_2(\text{Net}_2)_3$] are difficult due to the reasons already explained. [See diethylamino-tungsten(VI)fluorides and methoxy diethylamino tungsten(VI) fluorides.]

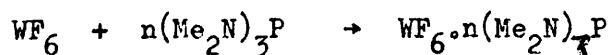
The reason the last fluorine could not be substituted in these reactions is not understood, particularly when the comparable compounds $\text{W}(\text{OMe})_6$, $\text{W}(\text{OPh})_6$; $\text{W}(\text{NMe}_2)_6$ and $\text{WCl}(\text{OMe})_5$ are known.^{59,61,89}

REACTION OF TRIS(DIMETHYLAMINO)PHOSPHINE WITH TUNGSTEN

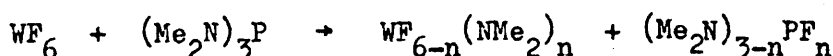
HEXAFLUORIDE

By analogy with its reactions with SOF_2 , SF_4 , PF_5 and PF_3 ^{69-71,91} tris(dimethylamino)phosphine, $(\text{Me}_2\text{N})_3\text{P}$ was expected to react with WF_6 in one of the three ways :

1. Reduction of W(VI) to W(V) or (IV)
2. Complex formation with WF_6



3. Substitution reaction with WF_6 to form dimethylamino-tungsten(VI)fluorides

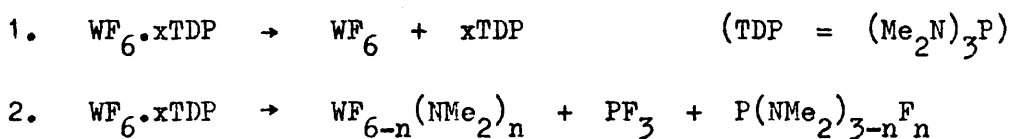


The first possibility, which would be accompanied by the oxidation

of P(III) to P(V), is most unlikely owing to the weak oxidising power of WF_6 . In fact no PF_5 , $\text{PF}_2(\text{NMe}_2)_3$ or related species are obtained in these reactions.

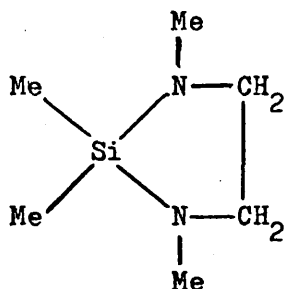
The reaction mixture containing $(\text{Me}_2\text{N})_3\text{P}$ and excess WF_6 solidifies to a light brown mass on shaking at 20° . On distillation of the volatiles from the reaction mixture (PF_3 and unreacted WF_6), most of the brown mass decomposes to $(\text{Me}_2\text{N})_3\text{P}$ and a viscous brown liquid. No suitable solvent could be found for the separation of the solid mass from viscous brown liquid. Analysis of the residue, in the reaction flask (after separating from $(\text{Me}_2\text{N})_3\text{P}$) corresponds to a mixture of $\text{WF}_{6-n}(\text{Net}_2)_n$ and $\text{WF}_{6-x} \cdot x(\text{Me}_2\text{N})_3\text{P}$ complex. The N.m.r. spectrum, of this residue in C_6F_6 in which it is slightly soluble, also suggests the presence of more than one species.

The results described above suggest the initial formation of some $\text{WF}_{6-x} \cdot x(\text{Me}_2\text{N})_3\text{P}$ complex in the reaction of WF_6 with $(\text{Me}_2\text{N})_3\text{P}$. This complex appears to decompose slowly according to :

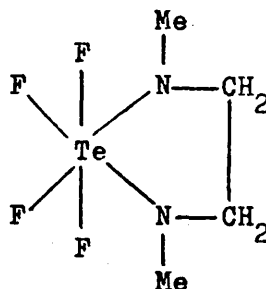


REACTION OF TRIMETHYLSILYL IMIDAZOLE WITH TUNGSTEN HEXAFLUORIDE

The reaction of tellurium hexafluoride with tetramethyl-1,3diaz-2-silacyclopentane (I) led to:

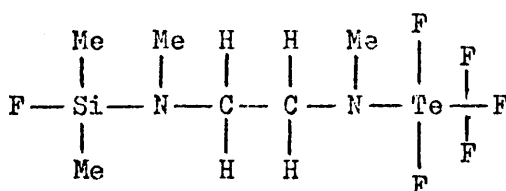


(I)



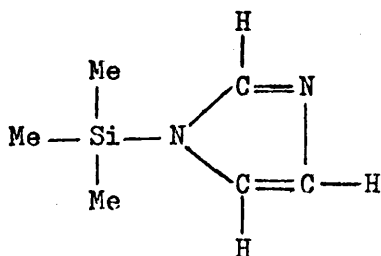
(II)

the formation of (III) rather than the expected product (II).⁶⁷

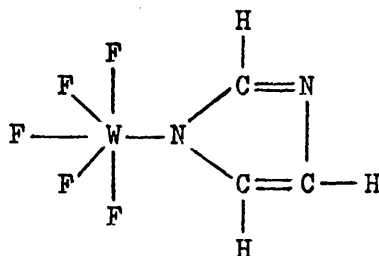


(III)

An attempt was made to carry out a comparable reaction with tungsten hexafluoride using trimethylsilyl imidazole (IV).



(IV)



(V)

Although Me_3SiF was identified, no evidence could be obtained for the expected product (V). The product from these reactions is a light brown solid insoluble in most of the common organic solvents such as C_6F_6 , CCl_3F , Me_4Si , CS_2 , CCl_4 , CHCl_3 , acetone, toluene, benzene and hexane. Analysis of the brown solid suggests the presence of more than one species. Owing to the lack of a suitable solvent, no spectroscopic studies were carried out on these compounds.

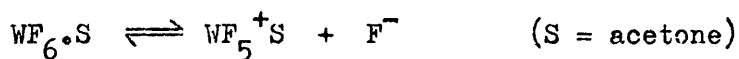
AMINOLYSIS OF TUNGSTEN HEXAFLUORIDE WITH DIETHYLAMINE

Tungsten hexafluoride reacts with diethylamine below 20° giving a light brown solid. Its elemental analysis corresponds to $\text{WF}_6 \cdot 1.5\text{Et}_2\text{NH}$, but its infra-red and n.m.r. spectra in acetone are more complicated than expected and suggest that some aminolysis has occurred. This is supported by the colour of the solid, since simple adducts of WF_6 with

primary and tertiary amines are colourless.^{39,40}

In an attempt to clarify the reaction of WF_6 with Et_2NH , conductometric titrations of WF_6 with Et_2NH were carried out in acetone solution. Reproducible results were obtained from two experiments using different initial concentrations of WF_6 and the plots of the variation of the specific conductance of the solutions with the mole ratio of amine : WF_6 are shown in Fig. 1.1.

The solution of tungsten hexafluoride in acetone shows an appreciable rise in conductivity compared with the pure solvent, and this can be explained by slight dissociation of the tungsten hexafluoride in equilibria of the type :



The yellow solution turns brown when amine is added, probably due to the formation of WF_5NEt_2 , and then is a rapid increase in conductivity which reaches a maximum when the mole ratio of amine : WF_6 is about 0.7. A rapid decrease in the conductance values is then observed until, at a mole ratio $\text{Et}_2\text{NH}:\text{WF}_6$ of about 1:1. the decrease becomes more gradual and a light green solid begins to precipitate from solution. Precipitation continues until the mole ratio is approximately 2:1. Elemental analysis of the light green solid, obtained in a separate experiment by treating WF_6 with excess of amine in acetone solution, corresponds to $\text{WF}_5\text{NEt}_2 \cdot \text{HNEt}_2 \cdot 0.5 \text{ acetone}$. The infra-red spectrum of the solid contains a weak, broad band, at approximately 3100 cm^{-1} , assigned to $\nu(\text{N-H})$, in addition to a strong band at 1708 cm^{-1} due to the complexed acetone.^{85a}

By comparing this reaction with the corresponding aminolysis reactions of titanium tetrafluoride with secondary amines,^{57,58} the following reaction scheme is proposed to account for the observations described above.

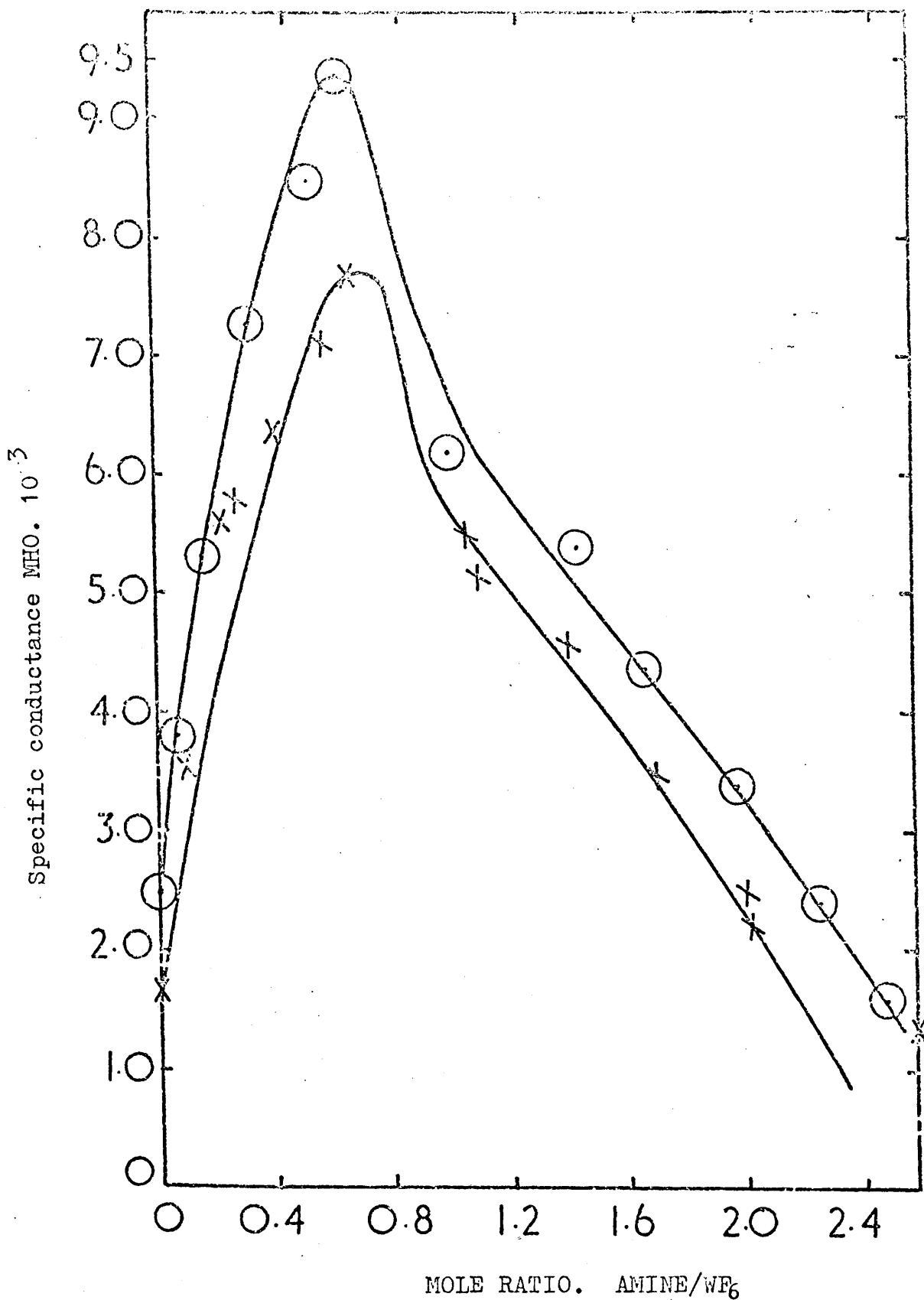
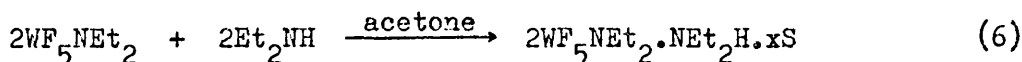
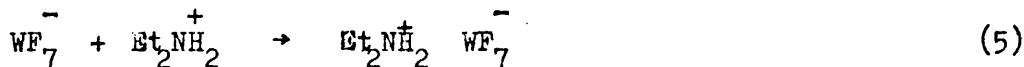
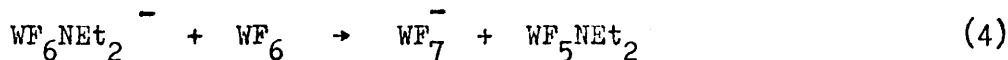
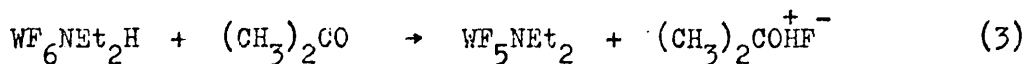
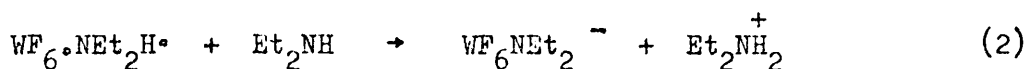
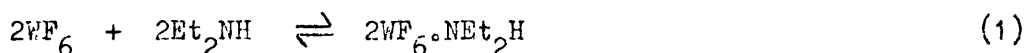


Fig. 1.1 - Conductometric titration of WF_6 solution in acetone with diethylamine: O = Experiment 1;
x = Experiment 2.



It is quite likely that some secondary reactions, such as the formation of $\text{Et}_2\text{NH}_2^+\text{F}^-$ also occur. Moreover, WF_5Net_2 has been found to decompose in acetone slowly and such reactions are also likely to complicate the reaction scheme. Hence in a reaction as complex as this, it is very difficult to propose any unique solution, especially on the basis of the limited experimental results available. To confirm the reaction scheme, a detailed study of the reaction involving a continuous variation study,^{57,58} conductometric titrations by the addition of WF_6 to an amine solution, complete analysis of the reaction products both solids and solutions is necessary.

CONCLUSIONS

Dialkylaminotungsten(VI)fluorides of the formula $WF_{6-n}(NR_2)_n$ [R = Me; n = 1; R = Et; n = 1, 2 and 4] are obtained from the stoichiometric reactions of Me_3SiNR_2 with WF_6 . $WF_3(NEt_2)_3$ is not obtained from these reactions, and the experiments aimed at its preparation give $WF_4(NEt_2)_2$ or a mixture of unidentified species instead. WF_5NR_2 and $WF_4(NEt_2)_2$ are believed to be associated, but $WF_2(NEt_2)_4$ appears to be monomeric in solution.

Diethylaminotungsten(VI)pentafluoride reacts with dimethylsulphite giving $WF_4(NEt_2)[OS(O)OMe]$ which slowly decomposes to $WF_4(NEt_2)(OMe)$. The tungsten-nitrogen bond is not cleaved by the reaction of WF_5NEt_2 with anhydrous HCl, substitution occurs instead. N.m.r. spectra of the products obtained from the reaction of WF_5NEt_2 with Me_3SiOMe or $Me_2Si(OMe)_2$ are consistent with the presence of more than one species. More work is needed to establish the oxidation number of W in chlorodialkylaminotungstenfluorides obtained from the reaction of WF_5NEt_2 with Me_3SiCl . These are also mixtures and are not properly characterized.

One $-NEt_2$ group in $WF_2(NEt_2)_4$ is replaced by OMe or Cl in its reaction with Me_3SiOMe and Me_3SiCl respectively. The products being $WF(OMe)_2(NEt_2)_3$ and $WCl_2(NEt_2)_3$. More work is required to understand the mechanisms of these reactions. Generally, diethylaminotungsten(VI)-fluorides are less reactive than WF_6 itself.

Tris(dimethylamino)phosphine forms a complex with WF_6 that decomposes to mixture of products which are not properly characterized. Trimethylsilyl imidazole reacts with WF_6 at 20° giving Me_3SiF but the tungsten containing species could not be characterized.

Aminolysis occurs in the reactions of WF_6 with diethylamine, and this

is supported by the conductometric titrations of WF_6 with diethylamine in acetone solution. More work is required to suggest a satisfactory reaction scheme for this reaction.

EXPERIMENTAL

Chemicals

AnalaR or spectroscopic grade solvents and reactants were used where available, others were purified by standard methods.⁹²

Tungsten hexafluoride (Allied Chemical Co.) was purified by low temperature trap to trap distillation over sodium fluoride. Particular attention was paid to the purification of the diethylaminotrimethylsilane (Aldrich) and dimethylaminotrimethylsilane (prepared from the reaction of trimethylchlorosilane and dimethylamine).⁹⁴ After several distillations at atmospheric pressure these were degassed and dried over activated Linde 4A molecular sieves, and finally distilled under vacuum. Their infra-red spectra were identical to those previously reported.⁹³ Trimethylmethoxysilane (Pierce Chemicals), dimethyldimethoxysilane (Aldrich), trimethylchlorosilane (B.D.H.) and dimethyl sulphite were all dried and stored over activated Linde 4A molecular sieves. Trimethylsilyl imidazole (Peninsular Chem. Research) and tris(dimethylamino)phosphine (Aldrich) were distilled several times at atmospheric pressure and then stored over activated Linde 4A molecular sieves in an inert atmosphere box. Dimethylamine (B.D.H.), twice distilled at -78° was kept one month over fresh sodium before use.

EXPERIMENTAL PROCEDURE

All preparations were carried out in a vacuum system that could be pumped to $\leq 10^{-4}$ mm mercury. By flaming out the apparatus to the softening point temperature of the glass, traces of moisture were rigorously excluded.

Reactants and products were weighed in glass vessels fitted with Teflon stop-cocks. Involatile reactants and products were handled in a Lintott inert atmosphere box in which the concentration of moisture was known to be less than 12 p.p.m.

Details of the apparatus and the instrumentation used are given in the Appendix.

Reaction of Tungsten Hexafluoride with Dimethylaminotrimethylsilane

(a) A mixture of WF_6 (18.8 mmole) and Me_3SiNMe_2 (12.1 mmole) reacted vigorously below 20° to give a dark brown viscous liquid, the reaction being completed within half an hour. The reaction proceeded more smoothly if the reactants were allowed to warm up slowly (from -196° to $20^\circ C$) over a period of 10 hours.

The fraction volatile at -80° was identified as Me_3SiF from its i.r. spectrum⁹⁵ and molecular weight determination. (Found 93.6; Me_3SiF requires 92.0). The i.r. spectrum of the fraction which was volatile at 20° corresponded to a mixture of Me_3SiF and unreacted WF_6 ,⁹⁶ but complete separation of WF_6 from Me_3SiF was not possible. Total weight of $WF_6 + Me_3SiF$. Found (two samples from separate experiments), 3.1 gm. and 3.7 gm. Required for 1:1 reaction 3.1 gm. and 3.8 gm. respectively.

As preliminary experiments had indicated that Me_3SiF was weakly complexed to diethylaminotungsten(VI)pentafluoride, WF_5NEt_2 , the residue a brown viscous liquid involatile at 20° , was pumped overnight to ensure the complete removal of the Me_3SiF .

The residue was formulated as dimethylaminotungsten(VI)pentafluoride from elemental analysis. Found (two samples from different experiments) C, 7.3, 7.2; H, 2.1, 1.8; N, 4.1, 4.4; F, 29.1, 29.6; W, 57.1, 56.7%

$C_2H_6F_5NW$ requires, C, 7.4; H, 1.9; N, 4.3; F, 29.4; W, 57.0%.

WF_5NMe_2 was insoluble in Me_4Si , CCl_3F , CS_2 , CCl_4 , $CHCl_3$ and cyclohexane. It was only very slightly soluble in hexafluorobenzene and toluene, while it decomposed in CH_3NO_2 , CH_3CN and acetone. The nature of the decomposition products was not investigated.

Due to its insolubility no information could be obtained from n.m.r. studies. On some occasions the 1H n.m.r. spectra gave a single peak of variable intensity at ~ 7.0 p.p.m., but this was supposed to be due either to slight hydrolysis or to an impurity.

Densities (of two different samples) of WF_5NMe_2 given in Table 1.5 were obtained from measurements in vacuum using a dilatometer calibrated with mercury.

Table 1.5

Densities of WF_5NMe_2 ($g.cm^{-3}$)

Temp. $^{\circ}C$	Sample I	Sample II
20	2.884	2.821
25	2.875	2.804
30	2.866	2.787
35	2.857	2.770
40	2.848	2.753
45	2.839	2.736
50	2.831	2.719

The equations representing these densities are $d = 2.92 - 0.00180 t$ and $d = 2.89 - 0.0034 t$ respectively, where d = density ($g.cm^{-3}$) and t = temperature ($^{\circ}C$).

Times of viscous flow, (for two different samples) measured using an Oswald viscometer adapted for vacuum use, were as follows: at 20°, 1020 and 1020; at 25°, 718 and 720; at 30°, 452 and 456 secs. The corresponding times for glycerol are 1914, 1227 and 810 secs. respectively. The measurements were made in a thermostated bath, which could be controlled to $\pm 0.5^\circ\text{C}$.

Infra-red spectrum (liquid film 4000-400 cm^{-1}) 3390w, 3260m, 3160w, 3035w, 2930w, 1720s, 1700sh, 1595m, 1451s, 1335s, 1255w, 1155w, 1145w, 1115w, 1070w, 1020s, 955m, 935sh, 873w, 855w, 818w, 705s, 645br,s, 600br,s, 502w, 465w, 435sh.

(b) Tungsten hexafluoride (3.5 mmol) and dimethylaminotrimethylsilane (9.3 mmol) reacted slowly at 0°. The reaction took more than 24 hours to reach completion. The volatile materials were identified as Me_3SiF and unreacted $\text{Me}_3\text{SiNMe}_2$ by i.r. spectroscopy,^{93,95} but no attempt was made to separate them. The residue was a brown sticky solid.

The solid was involatile at 20° and was hydrolysed immediately by water. It was insoluble in Me_4Si , CCl_3F , CS_2 , CCl_4 , CHCl_3 , C_6F_6 , toluene and hexane, and decomposed in CH_3NO_2 , CH_3CN and $(\text{CH}_3)_2\text{O}$.

Elemental analysis of the brown solid corresponded to a mixture of dimethylaminotungsten(VI)fluorides. Found, C, 11.0; H, 2.9; N, 6.4; F, 24.5; W, 54.0%. $\text{C}_4\text{H}_{12}\text{F}_4\text{N}_2\text{W}$ requires, C, 13.8; H, 3.5; N, 8.1; F, 21.8; W, 52.9%.

A detailed investigation of this reaction was not attempted, firstly, because pure products could not be isolated, and secondly, no solvent was available for spectroscopic studies of these compounds.

REACTIONS OF TUNGSTEN HEXAFLUORIDE WITH DIETHYLAMINO-
TRIMETHYLSILANE

(a) Formation of Diethylaminotungsten(VI)pentafluoride

The experimental procedure was similar to that used in the preparation of WF_5NMe_2 . The reactions leading to the formation of WF_5NEt_2 and the volatile products obtained are summarised in Table 1.6 together with the analysis of the WF_5NEt_2 samples obtained.

The involatile product from these reactions, in every case, was a dark red-brown viscous liquid. It was identified from its analysis (Table 1.6) as diethylaminotungsten(VI)pentafluoride, WF_5NEt_2 . It was hydrolysed readily by water and aqueous alkali. Its behaviour towards organic solvents was similar to that of WF_5NMe_2 , although it was slightly more soluble in C_6F_6 , toluene and octafluorotoluene.

The ^{19}F n.m.r. spectrum of WF_5NEt_2 in C_6F_6 consisted of a single weak peak at -128 ± 2 p.p.m. On one occasion this singlet was resolved to a doublet at -50° ($J_{\text{F-F}} = 60$ Hz.). The signal from the one fluorine atom trans to the $-\text{NEt}_2$ group, expected to be quintet, could not be detected even at -100° .

The ^1H n.m.r. spectrum of WF_5NEt_2 consisted of a triplet assigned to CH_3 - group at 1.1 ± 0.1 p.p.m., and a poorly resolved quartet at 5.7 p.p.m. assigned to WNCH_2 - group [$J_{(\text{CH}_3-\text{CH}_2)} = 7$ Hz.]. On some occasions the ^1H n.m.r. spectra also contained a sharp singlet at about 6.7 p.p.m., but this was ascribed to slight hydrolysis.

Densities (g.cm^{-3}) at various temperatures ($t^\circ\text{C}$) of two separate samples of WF_5NEt_2 are tabulated.

Table - 1.6

No.	Reactants (mmol)	Weight of WF ₆ + Me ₃ SiF after the reaction		Molecular Weight of Me ₃ SiF ^a	Analysis of brown liquid				
		Found	Required		Found	C (%)	H (%)	N (%)	F (%)
		(gms)	(gms)						
(1)	WF ₆ (16.8) + Me ₃ SiNEt ₂ (9.0)	3.2	3.2	93.7					
					C ₄ H ₁₀ F ₅ NW requires	13.7	2.9	4.0	27.0
						52.4			
(2)	WF ₆ (15.93) + Me ₃ SiNEt ₂ (15.9)	1.7	1.5	93.3					
						13.5	2.4	4.1	27.3
						52.0			
(3)	WF ₆ (11.4) + Me ₃ SiNEt ₂ (11.0)	1.8	1.1	-					
						14.0	3.1	4.1	26.6
						52.6			
(4)	WF ₆ (22.1) + Me ₃ SiNEt ₂ (22.2)	2.7*	2.04	94.8					
						15.9	3.0	4.1	27.3
						50.0			

a = molecular weight of Me₃SiF requires, 92.0; * = only Me₃SiF as identified from i.r. spectrum (Ref. 95)

Table 1.7

Densities (g.cm^{-3}) of WF_5NEt_2

Temp. °C	Sample I	Sample II
20	2.366	2.365
25	2.360	2.361
30	2.353	2.356
35	2.347	2.350
40	2.340	2.343
45	2.330	2.339
50	2.327	2.334

($d = 2.393 - 0.001334t$)

($d = 2.387 - 0.00107t$)

Times of viscous flow, (for two different samples) were as follows.

At 20°, 321 and 315; at 25°, 243 and 241; at 30°, 183 and 183 secs.

The corresponding times for glycerol were 1914, 1227 and 810 sec.

The infra-red spectrum of WF_5NEt_2 was as follows : (liquid film 4000-400 cm^{-1}) 3215s, 3130sh, 2985s, 2945m, 2881w, 1708sh, 1685w, 1589m, 1466sh, 1451s, 1392sh, 1381m, 1340w,br, 1311s, 1272v.w, 1185m, 1195w, 1124m, 1089s, 1064s, 1020s, 1000sh, 910sh, 895m, 855w, 797s, 779sh, 695s, 585-650s,br, 465w.

An attempt was made to determine the molecular weight of the sample, by measuring the lowering of the vapour pressure of C_6F_6 by WF_5NEt_2 , but owing to the slight solubility of WF_5NEt_2 no reasonable results could be obtained. Two different determinations gave the values of 158 and 646 respectively.

The thermal decomposition of WF_5NEt_2 was carried out in a glass vessel (200 ml. volume) fitted with a Teflon glass stop-cock. The progress of thermal decomposition was followed by recording changes in pressure. The flask containing WF_5NEt_2 was heated slowly to 100° but even after one hour no evidence for decomposition was found. The sample began to decompose at 120° but after the sample had been heated for about an hour at 200° the colour of the material in the flask remained unchanged suggesting that only slight decomposition had occurred. The decomposition products were identified from infra-red spectra as ethylene⁹⁷ and ethyl fluoride.⁹⁸ The residue left in the flask was identical in appearance with WF_5NEt_2 , but was found to be more stable in solvents such as CH_3NO_2 and CH_3CN . Analytical and spectroscopic evidence indicated that the W- NEt_2 group was still present. Elemental analysis of three samples obtained from three different experiments were as follows : found, C, 16.3 13.7 and 14.0; H, 3.3, 3.0 and 3.2; N, 3.8, 4.4 and 4.5; F, 25.7, 25.0 and 25.3; W, 50.5, 51.5 and 51.7% $\text{C}_4\text{H}_{10}\text{F}_4\text{NW}$ requires, C, 13.7; H, 2.9; N, 4.0; F, 27.0; W, 52.4%

The ^{19}F n.m.r. spectrum (in CH_3NO_2 or C_6F_6 , CCl_3F external standard), of this compound consisted of three signals at -141.3 (single line); -60 ± 2 (complex) and -33.0 (complex) p.p.m. The ^1H n.m.r. spectrum (in CH_3NO_2 , TMS external standard) consisted of a complex set of peaks at -1.13 p.p.m. assigned to $-\text{CCH}_3$ and -5.6 p.p.m. (complex) assigned to WNCH_2- and a very weak broad signal at -3.0 p.p.m.

Infra-red spectrum (liquid film $4000-400\text{ cm}^{-1}$) 3225m, 3170sh, 2995m, 2942w, 1590s, 1475sh, 1452m, 1430sh, 1392w, 1380w, 1332w, 1312s, 1160w, 1115w, 1055w, 1035w, 1015m, 990w, 772m, 695w.

Formation of Tetrakis(diethylamino)tungsten(VI)difluoride

The experimental procedure for the preparation of $\text{WF}_2(\text{NEt}_2)_4$ was

similar to that already described.

WF_6 (8.1 mmol) and $\text{Me}_3\text{SiNEt}_2$ (51.3 mmol) were allowed to react at 20° for 24 hours. Material volatile at 20° was identified as unchanged $\text{Me}_3\text{SiNEt}_2$ and Me_3SiF from its infra-red spectrum.^{93,95} Separation was not attempted. [Weight of $\text{Me}_3\text{SiNEt}_2$ + Me_3SiF . Found = 5.9 gm.; requires for 4:1 reaction, 5.7 gm.].

The residue was a brown, sticky solid involatile at 20° and quite different in behaviour from the other dialkylaminotungsten(VI)fluorides. It was characterized as tetrakis(diethylamino)tungsten(VI)fluoride, $\text{WF}_2(\text{NEt}_2)_4$.

Elemental analysis : found, C, 37.3; H, 7.7; F, 7.3; W, 36.7%
 $\text{C}_{16}\text{H}_{40}\text{F}_2\text{N}_4\text{W}$ requires, C, 37.7; H, 7.9; F, 7.5; W, 36.1%.

It was completely soluble in C_6F_6 and fairly soluble in CS_2 , toluene and octafluorotoluene. The molecular weight determinations, from the lowering in vapour pressure of C_6F_6 by $\text{WF}_2(\text{NEt}_2)_4$, were consistent with its being monomeric. The results are given in the Table 1.8.

Its infra-red spectrum (solid pressed between AgCl plates $4000\text{--}400\text{ cm}^{-1}$) was as follows : 3215s, 3130sh, 2995s, 2945s, 2889m, 1590s, 1465sh, 1415s, 1381s, 1335m, 1312s, 1275sh, 1185s, 1145w, 1130s, 1090s, 1065s, 1020sh, 1002s, 895s, 800s, 695s, 600br,s, 465m,br.

Preparation of Bis(diethylamino)tungsten(VI)tetrafluoride

The preparation of bis(diethylamino)tungsten(VI)tetrafluoride, $\text{WF}_4(\text{NEt}_2)_2$ was attempted by the three different methods described below :

(i) From WF_6 + $\text{Me}_3\text{SiNEt}_2$ (1:2 mole ratio)

A mixture of WF_6 and $\text{Me}_3\text{SiNEt}_2$ in 1:2 mole ratio was allowed to warm

up to 20° over a period of 12 hours to ensure complete reaction. The volatile fluoride was removed by distillation at 20° under vacuum, and was identified by infra-red spectroscopy and molecular weight determinations as Me_3SiF .

Table 1.8

Molecular weight of $\text{WF}_2(\text{NEt}_2)_4$

$\text{WF}_2(\text{NEt}_2)_4$ Molecular weight required if monomeric, 510		WF_5OMe^* Molecular weight required = 310	
Mole Fraction of $\text{WF}_2(\text{NEt}_2)_4$	Molecular Weight	Mole Fraction of WF_5OMe	Molecular Weight
0.152	562	0.118	358
0.117	564	0.073	341
0.075	566	0.060	344
0.065	556	0.050	328
0.052	558		

* WF_5OMe was used for the calibration of the apparatus, as it is known to be monomeric.⁸⁷

(ii) From WF_5NEt_2 and $\text{Me}_3\text{SiNEt}_2$ (1:1 mole ratio)

These reactions were very slow and took about 10 days at 20° to reach completion. The volatile product from these reactions was Me_3SiF identified from its infra-red spectrum⁹⁵ and molecular weight

determination.

(iii) From $\text{WF}_2(\text{NEt}_2)_4$ and excess WF_6

These reactions were very slow and took about 15 days at 20° to reach completion. A mixture of excess tungsten hexafluoride and $\text{WF}_2(\text{NEt}_2)_4$ was warmed to room temperature and kept for two weeks. The only volatile product from these reactions was unchanged WF_6 .

The analytical results, reaction details and products identified from routes (i), (ii) and (iii) are listed in Tables 1.9 and 1.9a.

(Pumping of the residue overnight was necessary to ensure the complete removal of volatiles from these compounds.)

In every case the involatile product was a dark red, highly viscous liquid involatile at 20° , characterized from analytical determinations (Table 1.9a) as bis(diethylamino)tungsten(VI)tetrafluoride, $\text{WF}_4(\text{NEt}_2)_2$. It was hydrolysed readily by water and alkali. Its behaviour towards common organic solvents was similar to that of WF_5NEt_2 although it was slightly soluble in CS_2 .

Considerable difficulty was experienced in obtaining ^{19}F n.m.r. signals for these compounds. A single peak signal (in C_6F_6 , CCl_3F external ref.) could only be obtained for one sample (product from reaction 2). ^1H n.m.r. chemical shifts vary from sample to sample (Table 1.9).

The infra-red spectrum of all the samples were similar. A typical spectrum (liquid film $4000\text{--}400\text{ cm}^{-1}$) was as follows : 3150w,br, 2985s, 2942m, 2883m, 2500w, 1595br,w, 1530s, 1455s, 1378m, 1350m, 1310m, 1276w, 1190m, 1141m, 1130w, 1090m, 1065m, 1042w, 1012m, 992s, 908m, 895m, 795m, 661w, 640m, 600s, 555w, 508w, 460w.

Densities of the samples of $\text{WF}_4(\text{NEt}_2)_2$ prepared by routes (i), (ii) and (iii) are given in Table 1.10 in order.

Table 1.9

No.	Reactants (mmol)	Method	Identified Products		Molecular Weight *		Weight of the		¹ H n.m.r. Chemical Shifts (p.p.m.)
			Found	Required	Found (mmol)	Required (mmol)			
							Volatiles		
(1)	WF ₆ (13.1) + Me ₃ SiNEt ₂ (26.1)	(i)	Me ₃ SiF WF ₄ (NEt ₂) ₂	91.7	92.0	32.6	26.1	--	
(2)	WF ₆ (14.5) + Me ₃ Si(NEt ₂)(29.1)	(i)	Me ₃ SiF WF ₄ (NEt ₂) ₂	93.0	92.0	29.1	29.1	1.3(t?); 4.2br ^x	
(3)	WF ₅ NEt ₂ (19.7) + Me ₃ SiNEt ₂ (19.6)	(ii)	Me ₃ SiF WF ₄ (NEt ₂) ₂	92.3	92.0	20.0	19.6	0.52br; 4.0br; 6.3(s) ^o	
(4)	WF ₂ (NEt ₂) ₄ (12.7) + WF ₆ (26.5)	(iii)	unchanged WF ₆ WF ₄ (NEt ₂) ₂	-	298	15.2	13.8	0.62br; 2.8br ^o	
(5)	WF ₂ (NEt ₂) ₄ (2.9) + WF ₆ (36.2)	(iii)	unchanged WF ₆ WF ₄ (NEt ₂) ₂	293	298	32.8	33.3	2.8br ^o	

* = of the volatiles; (t?) = poorly resolved appears to be a triplet; x = internal reference

br = broad; s = singlet; o = external reference

Table 1.9a

No.	<u>Elemental Analysis</u>					
	C	H	N	F	W	
	%	%	%	%	%	
	$C_8H_{20}F_4N_2W$					
	requires	23.8	5.0	6.9	18.8	45.5
1	Found	23.9	4.8	7.1	18.8	45.2
2		23.8	5.8	6.8	18.7	45.5
3		25.7	5.5	6.8	18.0	44.1
4		23.7	4.7	6.8	19.0	45.4
5		23.5	4.8	7.1	18.8	45.2

Table 1.10

Densities of $WF_4(NEt_2)_2$ ($d.gm.cm^{-3}$) at temperature t ($^{\circ}C$)

Temp. $^{\circ}C$	Sample I	Sample II	Sample III
20	1.972	2.157	2.103
25	1.966	2.151	2.097
30	1.956	1.146	2.091
35	1.953	2.140	2.085
40	1.946	2.135	2.079
45	1.940	2.130	2.073
50	1.933	2.124	2.067
	($d = 1.998 -$ $0.00136t$)	($d = 2.179 -$ $0.0011t$)	($d = 2.127 -$ $0.0012t$)

Table 1.11

No.	Reactants (mmol)	Reaction Conditions	Identified Products	Weight of the Volatiles	
				Found (gms)	Required for 1:3 reaction (gms)
(1)	$\text{WF}_6(4.1) + \text{Me}_3\text{SiNET}_2(12.1)$	20°C over 48 hours	Me_3SiF^a	1.3	1.1
			unchanged $\text{Me}_3\text{SiNET}_2^b$		
			$\text{WF}_4(\text{NET}_2)_2^c$		
(2)	$\text{WF}_6(6.1) + \text{Me}_3\text{SiNET}_2(18.4)$	20°C over 48 hours	Me_3SiF^a	-	-
			unchanged $\text{Me}_3\text{SiNET}_2^b$		
			$\text{WF}_4(\text{NET}_2)_2^c$		
(3)	$\text{WF}_6(9.6) + \text{Me}_3\text{SiNET}_2(32.3)$	20°C for 3 weeks	Me_3SiF^a	3.2	2.97
			unchanged $\text{Me}_3\text{SiNET}_2^b$		
(4)	$\text{WF}_6(4.8) + \text{Me}_3\text{SiNET}_2(14.2)$	20°C for 1 month	Me_3SiF^a Molecular weight	14.0	14.2(mmol)
			Found = 94.1 (mmol)		
			Me_3SiF Requires = 92.0		
(5)	$\text{WF}_6(?) + \text{Me}_3\text{SiNET}_2(\text{excess})$	20°C for 2 weeks	Me_3SiF^a	-	-
			unchanged $\text{Me}_3\text{SiNET}_2^b$		

(a,b = by infra-red spectroscopy
c = by analysis (Table 1.11a) (Ref. 93 & 95)

Viscosity and molecular weight determination could not be carried out due to the highly viscous nature of the compound and the lack of a suitable solvent.

ATTEMPTED PREPARATION OF TRIS(DIETHYLAMINO)TUNGSTEN(VI)TRIFLUORIDE

Reactions of WF_6 with Me_3SiNEt_2 in the mole ratio 1:3 were attempted, in order to prepare tris(diethylamino)tungsten(VI)trifluoride. Some of these reactions gave solids whose analyses correspond to $WF_4(NEt_2)_2$, while others appear to give mixtures. Reaction details, products identified and analytical results of the solids are summarised in Tables 1.11 and 1.11a.

Infra-red spectra of these products were similar. A typical spectrum (product from reaction 3) was as follows : (Nujol and fluorolube mulls, $4000-400cm^{-1}$). 3190s, 2995s, 2945s, 2890m, 1625w,br, 1375m, 1355w, 1300w, 1280w, 1230m, 1191s, 1150m, 1132sh, 1091w, 1070w, 1050w, 1010m, 895s, 851s, 795s, 575br,w, 480w, 430sh.

Table 1.11a

No.	Elemental Analysis					
	C	H	N	F	W	
	%	%	%	%	%	
Required for						
	$WF_3(NEt_2)_3$	31.5	6.6	9.2	12.5	40.2
	$WF_4(NEt_2)_2$	23.8	5.0	6.9	18.8	45.5
Found						
1		23.6	4.9	6.8	19.1	45.4
2		23.8	5.0	6.9	18.8	45.5
3		34.5	6.9	9.5	18.2	40.6
4		26.4	5.1	7.0	15.0	36.6
5		28.7	5.5	9.0	12.9	43.8

Detailed investigation of these compounds could not be carried out due to their highly viscous nature and the lack of a suitable solvent.

REACTIONS OF DIETHYLAMINOTUNGSTEN(VI)PENTAFLUORIDE

Reaction of Dimethyl Sulphite with Diethylaminotungsten(VI)pentafluoride

(a) WF_5NEt_2 (6.5 mmol) dissolved in dimethyl sulphite (6.4 mmol) at 20° . The solution was left at 20° for 72 hours. The volatile material was identified from its infra-red spectrum and molecular weight determination as MeF .⁹⁹ (Molecular weight found 37.4, MeF requires 34.0.)

The residue was a dark brown viscous liquid, involatile at 20° . It was soluble in C_6F_6 giving brown solution. It was formulated on the basis of elemental analysis as $\text{WF}_4(\text{NEt}_2)[\text{OS}(\text{O})\text{OMe}]$, Found, C, 17.2; H, 3.7; N, 3.4; S, 7.4; F, 18.3; W, 42.9% $\text{C}_5\text{H}_{13}\text{F}_4\text{O}_3\text{NW}$ requires C, 14.1; H, 3.1; N, 3.3; S, 7.5; F, 17.9; W, 43.1%

The brown liquid was found to decompose slowly at 20° but rapidly at 100° to give SO_2 and MeF .⁹⁹

The ^1H n.m.r. spectrum of the compound $\text{WF}_4(\text{NEt}_2)[\text{OS}(\text{O})\text{OMe}]$ (1) contained three broad signals at 5.4, 3.1 and 1.3 p.p.m. in addition to a sharp single line signal at 3.6 p.p.m. Its ^{19}F n.m.r. spectrum consisted of a poorly resolved, weak signal at -59.8 p.p.m. which appeared to be a doublet.

The infra-red spectrum of the product (I) (liquid film $4000\text{--}400\text{ cm}^{-1}$) was as follows : 3100br,w, 2995w, 2960s, 2890w, 2840w, 1460s, 1390w, 1315w, 1210s, 1069w, 975sh, 960s, 800w, 739m, 695s, 620s, 590m, 455w, 415w.

(b) The above reaction was repeated, under similar conditions, with 9.6 mmol of WF_6 and 12.1 mmol of $(\text{MeO})_2\text{S} = \text{O}$. Sulphur dioxide was

was identified in addition to MeF and brown liquid.⁹⁹

The involatile brown liquid appeared to be different from the one obtained in the above reaction as it was only slightly soluble in C_6F_6 . Its analysis corresponded to methoxydiethylaminotungsten(VI)tetrafluoride, $WF_4 \cdot (NEt_2)(OMe)$. Found, C, 16.3; H, 3.5; N, 3.8; F, 21.4; W, 50.5% $C_5H_{13}F_4ONW$ requires, C, 16.5; H, 3.6; N, 3.9; F, 21.0; W, 50.7%.

The 1H n.m.r. spectrum of $WF_4(NEt_2)(OMe)$ (II) contained three broad bands at 5.2, 2.9 and 1.2 p.p.m. in addition to a sharp singlet at 3.5 p.p.m. Its ^{19}F n.m.r. spectrum consisted of three poorly resolved multiplets at -61.3, -51.0 and -34.9 p.p.m.

The infra-red spectrum of the product was as follows : (liquid film 4000-400 cm^{-1}) 3100br,w, 2980w, 2920w, 2880w, 2850w, 2500m, 2400w, 1608s, 1450s, 1395sh, 1378m, 1372w, 1312s, 1190m, 1159m, 1132m, 1060m, 1038m, 1010w, 995s, 975sh, 908s, 870w, 793s, 694w, 680s, 620sh, 590s,br, 460br,w.

(c) Some other reactions with the $WF_5:NEt_2:(MeO)_2S=O$ ratio ranging from 1:1 to 1:4 were also attempted. Analysis of the products from latter reactions suggested the presence of more than one species. Their solubility in C_6F_6 varied from sample to sample but was greater in all cases than product (II). They all decomposed at 100° to SO_2 , MeF and blue solids. Their 1H and ^{19}F n.m.r. spectra were consistent with the analytical results and indicated the presence of both product (I) and (II) in addition to some unidentified species. Their i.r. spectrum was similar to that of product (I).

REACTION OF DIETHYLAMINOTUNGSTEN(VI)PENTAFLUORIDE WITH
DIMETHYLDIMETHOXSILANE

(a) WF_5NET_2 (4.8 mmol) and dimethyldimethoxysilane (28.7 mmol) were left at 20° for 24 hours. The volatile material removed at -80° was identified from its infra-red spectrum¹⁰⁰ and molecular weight determination as dimethyldifluorosilane, Me_2SiF_2 . Molecular weight found, 98.0; Me_2SiF_2 requires 96.0. The fraction volatile at 20° was a mixture of $\text{Me}_2\text{Si(OMe)}_2$ and Me_2SiF_2 as identified from its infra-red spectrum.^{100,101} Molecular weight determinations of the latter fraction suggested, however, that there was only a small quantity of Me_2SiF_2 . Molecular weight found, 119.6; $\text{Me}_2\text{Si(OMe)}_2$ requires 120.0; Me_2SiF_2 requires 96.0.

The residue was a red viscous liquid involatile at 20° and similar in appearance to WF_5NET_2 . Its elemental analysis corresponded to methoxydiethylaminotungsten(VI)tetrafluoride, $\text{WF}_4(\text{NET}_2)(\text{OMe})$. Found, C, 16.5; H, 3.6; N, 4.1; F, 22.5; W, 50.9%. $\text{C}_5\text{H}_{13}\text{F}_4\text{ONW}$ requires, C, 16.5; H, 3.6; N, 3.9; F, 21.0; W, 50.7%.

This compound was insoluble in most of the common organic solvents and was only slightly soluble in C_6F_6 . Its ^{19}F n.m.r. spectrum consisted of a singlet at 16.2 p.p.m. (CCl_3F external reference). No ^1H n.m.r. signals could be obtained for this compound.

The infra-red spectrum of $\text{WF}_4(\text{NET}_2)(\text{OMe})$ in the region $(4000-400)\text{cm}^{-1}$ was as follows : (liquid film) 3140w,br, 2975m, 2925s, 2881w, 2825s, 2510m, 1615w, 1525w, 1410s, 1390w, 1375m, 1350w, 1300m, 1180w, 1150m, 1050br,s, 960m, 900m, 790m, 695s, 671s, 650-590s,br, 515m, 450m.

(b) WF_5NET_2 (9.5 mmol) was shaken with $\text{Me}_2\text{Si(OMe)}_2$ (44.5 mmol) at 20° for 48 hours. Two layers were observed. A red viscous liquid

separated from a clear liquid.

The fraction volatile at -80° was identified from its infra-red spectrum¹⁰⁰ and molecular weight determination as Me_2SiF_2 . Molecular weight found 97.4, required for Me_2SiF_2 , 96.0. The other fraction volatile at 20°C was unchanged $\text{Me}_2\text{Si}(\text{OMe})_2$. Molecular weight found 118.5, required, 120.

The residue was a dark red viscous liquid involatile at 20° . It was hydrolysed readily by water and alkali and its solubility in organic solvents was similar to that already described. On the basis of elemental analysis it was formulated as trimethoxydiethylaminotungsten(VI)-difluoride. Found, C, 21.5; H, 5.1; N, 3.4; F, 9.2; W, 47.6%. $\text{C}_7\text{H}_{19}\text{F}_2\text{O}_3\text{NW}$ requires, C, 21.7; H, 4.9; N, 3.6; F, 9.8; W, 47.5%.

No ^{19}F n.m.r. signals were obtained for this compound and the ^1H n.m.r. (C_6F_6 solution, Me_4Si external standard) spectrum consisted of the following signals, (chemical shifts in p.p.m.). 1.2(c), 2.8(c), 4.3(s), 4.4(s), 4.5(c), 4.6br, 6.98(s).

Its i.r. spectrum (liquid film $4000\text{--}400\text{ cm}^{-1}$) was similar to that of $\text{WF}_4(\text{NET}_2)(\text{OMe})$, and was as follows : 3125w, 3040br,w, 2980sh, 2930m, 2880sh, 2825s, 2500m,br, 1600br,w, 1529s, 1450br,s, 1390w, 1375sh, 1308s, 1155w, 1050br,s, 990w, 960w, 900m, 795m, 738m, 550br,s, 470br,w.

REACTION OF TRIMETHYLMETHOXYSILANE WITH DIETHYLAMINOTUNGSTEN-(VI)PENTAFLUORIDE

(a) Me_3SiOMe (18.9 mmol) and WF_5NET_2 (9.0 mmol) were allowed to warm up slowly to 20° . Since no reaction appeared to have taken place, the reaction mixture was shaken for a further 48 hours at 20° . Initially WF_5NET_2 seemed to dissolve in Me_3SiOMe , then a black sticky solid was

deposited at the bottom of the flask. The volatiles were distilled off at 20° and were identified by infra-red spectroscopy as $\text{Me}_3\text{SiF}^{95}$ and unchanged $\text{Me}_3\text{SiOMe}^{101}$. Their separation was not attempted.

The residue, a black sticky solid involatile at 20°, was formulated from elemental analysis as methoxydiethylaminotungsten(VI)-tetrafluoride, $\text{WF}_4(\text{NEt}_2)(\text{OMe})$. Found, C, 15.2; H, 3.6; N, 3.7; F, 19.4; W, 51.9%. $\text{C}_5\text{H}_{13}\text{F}_4\text{ONW}$ requires, C, 16.5; H, 3.6; N, 3.9; F, 21.0; W, 50.7%.

It was insoluble in most of the common organic solvents mentioned above, and was only slightly soluble in C_6F_6 . Its ^1H n.m.r. spectrum contained the following signals in addition to the signals characteristic of $-\text{NEt}_2$ group⁸⁶ at 0.78 and 4.6 p.p.m.

4.0(s), 4.2(c) and 4.4(c) (p.p.m.)

Its ^{19}F n.m.r. spectrum consisted of two signals (both single lines) at -20.0 and +18.2 p.p.m.

The i.r. spectrum of $\text{WF}_4(\text{NEt}_2)(\text{OMe})$ (liquid film 4000-400 cm^{-1}) was as follows : 3150br,m, 2980s, 2940m, 2880m, 2835sh, 1650m, 1590w, 1530s, 1450s, 1375m, 1350w, 1310s, 1190w, 1140w, 1060s, 991s, 905m, 792s, 730w, 680sh, 660m, 580br,s, 460m.

(b) WF_5NEt_2 (8.8 mmol) and Me_3SiOMe (55.3 mmol) after shaking at 20° for 48 hours gave the same type of black sticky solid as the one obtained previously. Me_3SiF and unreacted $\text{Me}_3\text{Si(OMe)}$ were identified by infra-red spectroscopy.^{100,101}

Elemental analysis of the solid suggested that it was dimethoxydiethylaminotungsten(VI)trifluoride, $\text{WF}_3(\text{NEt}_2)(\text{OMe})_2$. Found C, 18.3; H, 4.2; N, 3.7; F, 14.6; W, 47.0%. $\text{C}_6\text{H}_{16}\text{F}_3\text{O}_2\text{NW}$ requires C, 19.2; H, 4.3; N, 3.7; F, 15.2; W, 49.0%.

The ^1H n.m.r. spectrum of this compound consisted of two singlets

at 4.0 and 4.15 p.p.m., and a doublet at 4.25 p.p.m. ($J_{H-H} = 2 \text{ Hz.}$), in addition to two broad signals at 0.76 and 4.34 p.p.m. assigned to $-\text{NEt}_2$ group.⁸⁶

The ^{19}F n.m.r. spectrum contained two major signals at 18.0 and 42.3 p.p.m. (both single lines). Assignment of these signals was not possible because of the absence of any fine structure.

Its i.r. spectrum (liquid film 4000-400 cm^{-1}) contained the following bands : 3125w, 3040brw, 2980sh, 2930m, 2880sh, 2825s, 2500m,br, 1600br,w, 1529s, 1450br,s, 1390w, 1375sh, 1308s, 1155w, 1050br,s, 990w, 960w, 900m, 795m, 738m, 550br,s, 470br,w.

Reactions Followed by N.M.R. Spectroscopy

(a) From a reaction of WF_5NEt_2 with approximately five fold excess of Me_3SiOMe a sample was removed after 20 hours and the variation of the ^{19}F and ^1H n.m.r. spectra with time was studied. The results are summarised in Tables 1.12 and 1.12b.

(b) A sample of the mixture was removed after 2 weeks from a reaction of WF_5NEt_2 with approximately five fold excess of Me_3SiOMe and gave the following ^1H n.m.r. spectrum (chemical shifts in p.p.m.) : 1.5br ($-\text{CCH}_3$), 4.9(s) (SiOMe), 5.0(s) ? , 5.2br,w (WNCH_2-), 5.4br (WNCH_2-), 7.2(s) impurity.

The ^{19}F n.m.r. spectrum of this solution consisted of two signals (both single lines) at -48.3 and 21.3 p.p.m.

(c) A sample of the mixture from a reaction of WF_5NEt_2 with approximately six fold excess of Me_3SiOMe , removed after a week and gave the following ^1H n.m.r. signals (chemical shifts in p.p.m.) 1.4 ($-\text{CCH}_3$), 4.6(s) (SiOMe), 4.8(c) ($\text{WNCH}_2 - ?$) 7.2(s) impurity.

Its ^{19}F n.m.r. spectrum contained the following signals (chemical shifts in p.p.m.) -142.2(s) ? , -120.0(s) (WF_5NEt_2 ?), -50.0(s) ? , +14.0(s) ? and +23.0(s) ? .

Table 1.12

¹H chemical shifts in p.p.m.

After 20 hours	After 4 days	After 10 days
1.0br (-CCH ₃)	0.9br (-CCH ₃)	1.4br (-CCH ₃)
3.2(s) (WOMe)	4.35(s) ?	4.9(s) (SiOMe)
3.9(s) (WOMe)	4.44(s) ?	5.0(s) ?
4.8(s) (SiOMe)	4.6br (WNCH ₂ -)	5.2br (WNCH ₂ -)
5.2br (WNCH ₂ -)	4.9(s) (SiOMe)	5.4br (WNCH ₂ -)
6.5(s) impurity	6.6(s) impurity	7.2(s) impurity

Table 1.12b

¹⁹F chemical shifts in p.p.m.

After 20 hours	After 4 days	After 10 days
-131.4(d) WF ₅ NEt ₂ ? (J _{F-F} = 65 Hz.)		-39.7(s) ?
-67.4(t) ? (J _{F-F} = 65 Hz.)	-43.4(s) ?	-24.7(s) ?
-53.4(t) ? (J _{F-F} = 65 Hz.)	-15.9(s) ?	+22.0(s) ?

REACTION OF ANHYDROUS HYDROGEN CHLORIDE WITH DIETHYLAMINO-
TUNGSTEN(VI)PENTAFLUORIDE

Anhydrous hydrogen chloride (50 cm. pressure) was allowed to react with WF_5NET_2 (15.24 mmol) at 20° for 24 hours. HCl was dried by distilling three times through -100° traps before reacting with WF_5NET_2 . The reaction was performed in a 500 ml. flask fitted with a Teflon stopcock. Volatiles were distilled at 20° and identified by infra-red spectroscopy to be unreacted HCl and SiF_4 .^{97,102} SiF_4 was presumably formed by the action of HF on the glass.

The residue, a black viscous liquid, was involatile at 20° and was more stable towards hydrolysis than WF_5NET_2 . It was found to be contaminated with an orange powder. Separation by solvent extraction was attempted, but was not successful. The black liquid was insoluble in C_6F_6 , TMS, CCl_3F , CCl_4 , CHCl_3 , CS_2 , toluene and hexane. Elemental analysis of the liquid was consistent with the presence of more than one species. Found C, 14.5; H, 3.5; N, 4.3; F, 18.9; Cl, 13.8; W, 43.4%.

Atomic ratio, C:H:N:F:Cl:W = 5.1:14.8:1.3:4.2:1.7:1.

Its i.r. spectrum (liquid film $4000\text{--}400\text{ cm}^{-1}$) was as follows :
3100br,w, 2910s, 2845m, 1560m,br, 1525w, 1472w, 1450m,br, 1175w, 1150w,
1055w, 985w, 870w, 760w, 675w, 600s.

No n.m.r. studies were possible owing to the lack of a suitable solvent.

REACTION OF TRIMETHYLCHLOROSILANE WITH DIETHYLAMINOTUNGSTEN-
(VI)PENTAFLUORIDE

Various reactions of WF_5NET_2 and Me_3SiCl were carried out (Table 1.13).

Table 1.13

Summary of the reactions

No.	Reactants (mmol)	Reaction Conditions	Products
1	WF ₅ NEt ₂ (5.0) + Me ₃ SiCl (30.0)	100° for 24 hours	Me ₃ SiF ^a unchanged Me ₃ SiCl recovered Black sticky solid contaminated with a yellow powder
2	WF ₅ NEt ₂ (6.4) + Me ₃ SiCl (23.0)	Shaken at 20° for 48 hours	Me ₃ SiF ^a Molecular weight Found = 94.2 Me ₃ SiF Requires = 92.0 Weight of Me ₃ SiF Found = 22.8 mmol Required for completion of the reaction= 23.0 mmol Residue same as above
3	WF ₅ NEt ₂ (19.6) + Me ₃ SiCl (83.0)	Shaken at 20° for 96 hours	Me ₃ SiF ^a unchanged Me ₃ SiCl recovered (residue same as above)
4	WF ₅ NEt ₂ (8.8) + Me ₃ SiCl (50.0)	Shaken at 20° for 200 hours	Me ₃ SiF ^a unchanged Me ₃ SiCl recovered (residue same as above)

^a = by i.r. spectroscopy (Ref. 95)

The products were all black sticky solids which were difficult to handle. They were similar to those obtained from the reaction of WF_5NEt_2 and HCl . They were insoluble in C_6F_6 , toluene, CHCl_3 , CCl_4 , CS_2 , CCl_3F , Me_4Si , and hexane. They were probably mixtures, but because of handling difficulties their separation was not attempted. The elemental analysis of the products is given in Table 1.13b.

Table 1.13b

Elemental analysis of the various products from the above reactions

No.		C (%)	H (%)	N (%)	Cl (%)	F (%)	W (%)
1	Found	12.4	2.6	4.6	34.1	3.2	42.8
	Ratio	(6.1)	(15.5)	(2.0)	(5.7)	(1)	(1.4)
	$\text{WFCl}_4\text{NEt}_2$ requires	11.5	2.4	3.4	34.1	4.6	44.1
2	Found	12.6	2.6	3.8	29.5	5.8	45.0
	Ratio	(4.3)	(10.4)	(1.1)	(3.4)	(1.3)	(1.0)
3	Found	11.7	3.6	3.1	34.2	2.2	45.3
	Ratio	(8.5)	(31.0)	(2.0)	(8.4)	(1.0)	(2.1)
4	Found	12.1	2.6	3.3	35.8	0.4	45.8
	Ratio	(4.3)	(11.0)	(1)	(4)	(-)	(1)
	WCl_4NEt_2 requires	(12.0)	(2.5)	3.5	35.7	-	46.0

All of these products reduced acidified KMnO_4 solutions. In a quantitative estimation of the sample from last reaction 0.374 gm. of the sample were found to be equivalent to 2.2×10^{-6} mole of KMnO_4 . This corresponded to an oxidation number of tungsten 3.7.

Due to the lack of a suitable solvent no n.m.r. signals were observed except in first case, where a singlet at +26.5 p.p.m. was observed in the ^{19}F n.m.r. spectrum and a broad peak in ^1H n.m.r. spectrum at -3.75 p.p.m.

The infra-red spectra of all the samples was similar and contained the following absorptions (solid pressed between KBr plates, 4000-400 cm^{-1}) 3160br,s, 2980s, 2939s, 2880sh, 2435w, 2340w, 2240w, 2120w, 1705s, 1685sh, 1635w, 1575s, 1529s, 1445s, 1415w, 1390w, 1375w, 1360w, 1340sh, 1320w, 1275s, 1185w, 1155w, 1125w, 1080m, 1050m, 1010sh, 985s, 942m, 885s, 789s, 755s, 610br,m, 580sh, 510w, 460w.

These compounds when dissolved in water gave light brown solutions compared with the blue of dialkylaminotungsten(VI)fluorides.

BEHAVIOUR OF CARBON DISULPHIDE AND METHANOL TOWARDS WF_5Net_2 AND $\text{WF}_2(\text{Net}_2)_4$

WF_5Net_2 was not miscible with CS_2 even on shaking and was decomposed in methanol.

$\text{WF}_2(\text{Net}_2)_4$ dissolved in CS_2 . It appeared to react slowly with methanol (see n.m.r. spectrum Table 1.4) but products could not be identified.

REACTIONS OF TETRAKIS(DIETHYLAMINO)TUNGSTEN(VI)DIFLUORIDE

(i) WITH TRIMETHYLCHLOROSILANE

A mixture of Me_3SiCl (39.1 mmol) and $\text{WF}_2(\text{Net}_2)_4$ (10.7 mmol) was

allowed to warm from -196° to 20° over a period of 4 hours. There was no visual evidence of any reaction. On shaking, $\text{WF}_2(\text{NEt}_2)_4$ appeared to dissolve slowly in Me_3SiCl , and after a week's shaking a black sticky solid settled at the bottom of the flask. The volatiles from this reaction were identified as $\text{Me}_3\text{SiF}^{95}$ and unchanged $\text{Me}_3\text{SiCl}^{103}$ from infra-red spectroscopy. Another compound was suspected to be present among the volatiles from inspection of the infra-red spectrum of the volatiles. But it could not be identified by n.m.r. and mass spectroscopic measurements. Its n.m.r. gave no signals at all while its mass spectrum contained the following main peaks corresponding to $m/e = 26-29, 31, 32, 39, 41-43, 45, 47, 49, 56, 57, 59, 63, 66, 71-81, 87, 93, 95, 118, 123, 133, 146, 154, 160, 171$.

The residue, a black sticky solid involatile at 20° , was soluble in C_6F_6 . It was formulated from its elemental analysis as dichloro-tris(diethylamino)tungsten(VI)monofluoride, $\text{WFCI}_2(\text{NEt}_2)_3$. Found, C, 27.7; H, 5.9; N, 8.7; Cl, 15.1; F, 3.8; W, 38.6% $\text{C}_{12}\text{H}_{30}\text{Cl}_2\text{FN}_3\text{W}$ requires C, 29.4; H, 6.1; N, 8.6; Cl, 14.5; F, 3.9; W, 37.6%

Its ^1H n.m.r. spectrum in C_6F_6 contained the signals assigned to $-\text{NEt}_2$ group, (by comparison with the chemical shifts of $\text{WF}_2(\text{NEt}_2)_4$) at 0.9 and 4.6 p.p.m. Its ^{19}F n.m.r. spectrum consisted of two signals, one at +15.0 p.p.m. (single line) assigned to some unreacted $\text{WF}_2(\text{NEt}_2)_4$, and another at -46.7 (single line) p.p.m. An ^{19}F n.m.r. spectrum could only be obtained for one sample

The i.r. spectrum of $\text{W(F)Cl}_2(\text{NEt}_2)_3$ (solid pressed between KBr plates, $4000-400\text{ cm}^{-1}$) contained the following absorptions: 3260v.w, 3085m, 2980s, 2940m, 2875w, 2825v.w, 2685w, 2475m, 1525s, 1455s, 1375w, 1355w, 1325w, 1295m, 1275sh, 1185m, 1139s, 1089s, 1065m, 1000br,s, 892s, 842w, 799s, 772w, 589w, 520m, 455w.

(ii) REACTION OF TRIMETHYLMETHOXY-SILANE WITH TETRAKIS-(DIETHYLAMINO)TUNGSTEN(VI)TETRAFLUORIDE

$\text{WF}_2(\text{NET}_2)_4$ (6.7 mmol) dissolved readily in Me_3SiOMe (42.4 mmol) giving a blood-red solution. The solution was shaken for 2 weeks at 20° to ensure the completion of the reaction. Volatiles from this reaction were identified by infra-red spectroscopy as Me_3SiF ,⁹⁵ unchanged Me_3SiOMe ¹⁰¹ and an unidentified liquid.

The residue was a brown viscous liquid involatile at room temperature. It was soluble in C_6F_6 and was formulated as dimethoxytris(diethylamino)-tungsten(VI)monofluoride, $\text{WF}(\text{OMe})_2(\text{NET}_2)_3$, on the basis of its elemental analysis. Found (two samples from different experiments) C, 33.1 and 29.9; H, 6.8 and 6.6; N, 8.7 and 8.5; F, 7.9 and 4.0; W, 39.4 and 38.2%. $\text{C}_{14}\text{H}_{36}\text{F}_2\text{O}_2\text{N}_3\text{W}$ requires C, 34.9; H, 7.7; N, 8.7; F, 4.0; W, 38.2%.

The ^1H n.m.r. spectrum of the residue (C_6F_6 solution, TMS external reference) contained the following signals (chemical shifts in p.p.m.) : $1.1 \pm 0.05(\text{t?})$ (CCH_3); $3.3(\text{s})$ (WOMe),⁸⁶ $4.35 \pm 0.15\text{br}$ (WNCH_2).

Its ^{19}F n.m.r. spectrum consisted of only one signal (single line) at +63.7 p.p.m. (CCl_3F internal standard), (comparison with $\text{WF}(\text{OMe})_5$ which has a signal at +39.5 p.p.m.). ^{19}F n.m.r. signal could only be observed for one sample. Its i.r. spectrum (liquid film $4000\text{--}400\text{ cm}^{-1}$) was as follows : 2970s, 2955s, 2870s, 2809m, 1530s, 1462sh, 1450m, 1425sh, 1370m, 1348m, 1300w, 1189m, 1139m, 1075m, 1060s, 1000s, 890s, 790s, 560m, 540s, 485s.

REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIS(DIMETHYLAMINO)-PHOSPHINE

WF_6 (14.4 mmol) was distilled on to tris(dimethylamino)phosphine

(TDP) (13.6 mmol) under vacuum. The reaction mixture was allowed to warm from 196° to -80° and then to 20° over a period of twelve hours. A thin red crust formed at the top of a colourless liquid. It was thought that the reaction was very slow and needed vigorous conditions. The flask was shaken and within minutes its contents solidified to a light brown mass. On distilling the volatiles, the solid appeared to decompose (assumed from the white dense fumes coming off flask leaving behind a clear liquid). On warming the flask containing the volatiles, a dark red liquid separated from a pale yellow liquid. The red viscous liquid was involatile at 20° . The colourless liquid was identified from infra-red spectroscopy as a mixture of PF_3 ¹⁰⁴ and WF_6 .⁹⁶ The light yellow liquid left in the reaction flask was identified as unreacted tris(dimethylamino)phosphine by comparing its infra-red and n.m.r. spectra with those of the pure compound.

The red viscous liquid left in the second flask was in small quantity and was used for analysis.

Elemental Analysis. Found, C, 19.5; H, 5.1; N, 11.3; F, 19.5; W, 49.1; P, 6.2% $\text{WF}_3[\text{N}(\text{CH}_3)_2]_3$, requires C, 19.3; H, 4.8; N, 11.3; F, 15.2; W, 49.3; P = 0%.

(b) WF_6 (18.1 mmol) and tris(dimethylamino)phosphine (9.35 mmol) were reacted at 20° for 2 weeks. A thin, brown-yellow crust formed at the top of a light yellow liquid during this time. Volatiles were distilled at 20°C from the reaction flask. These were identified as PF_3 and unreacted WF_6 from infra-red spectroscopy.^{96,104}

The residue, involatile at 20° was a dark-red viscous liquid and a pale yellow liquid. The brown viscous liquid was separated from the yellow liquid by decantation and was later dried by pumping for two days.

The light yellow liquid was identified from its infra-red and n.m.r. spectra to be unchanged $(\text{Me}_2\text{N})_3\text{P}$.

The brown liquid was slightly soluble in hexafluorobenzene. Its ^{19}F n.m.r. spectrum consisted of one weak signal at -143 p.p.m. (single line), and its ^1H n.m.r. spectrum contained three signals at 5.0 (single line), 2.9 (poorly resolved doublet) and 1.9 (single line) p.p.m. These results were consistent with the presence of more than one species.

Elemental Analysis. Found C, 10.9; H, 3.3; N, 6.8; F, 28.4; W, 49.5; P, 1.1%.

The i.r. spectrum of brown mass (liquid film 4000-400 cm^{-1}) was as follows : 3500br,w, 3250br,w, 3030w, 2930s, 2870w, 2835w, 2790w, 1590w, 1525s, 1450(s), 1420w, 1400w, 1325m, 1295w, 1238m, 1165w, 1120w, 1065w, 1020m, 990w, 950s, 865sh, 843s, 777w, 731m, 695w, 600br, 480w, 430m.

REACTION OF TRIMETHYLSILYL IMIDAZOLE WITH TUNGSTEN HEXAFLUORIDE

Tungsten hexafluoride (9.8 mmol) was distilled on to trimethylsilyl imidazole (15.6 mmol) in a flask fitted with a 'Teflon' stop-cock. The flask was slowly allowed to warm from liquid nitrogen temperature to 20° . Two immiscible layers separated out in the flask and after about half an hour, light brown fumes appeared. The flask was cooled immediately to liquid nitrogen temperature. After warming the flask again, a minute quantity of a light brown solid appeared at the bottom. The flask was left at 20° for 24 hours and the quantity of the solid increased considerably. Volatiles were distilled off at 20° and were identified by infra-red spectroscopy to be $\text{Me}_3\text{SiF}^{95}$ and SiF_4^{102} .

The residue, a light brown solid, involatile at 20° was completely

insoluble in CH_3CN , CH_3NO_2 , CCl_4 , CHCl_3 , C_6F_6 , CS_2 , toluene, hexane and acetone.

Its elemental analysis (two samples from different experiments) did not correspond to a single product. Found, C, 14.5, 20.2; H, 2.0, 2.9; N, 14.0, 13.4; F, 23.7, 18.3; W, 45.5, 44.2%.

REACTION OF TUNGSTEN HEXAFLUORIDE WITH DIETHYLAMINE

A mixture of tungsten hexafluoride (30.5 mmol) and diethylamine (15.11 mmol) was kept at -60° for about six hours. The colour of the mixture changed from colourless through red to purple and brown fumes appeared in the reaction flask. The flask was maintained at -60° for a further 24 hours. The only volatiles obtained from the reaction were SiF_4 and unreacted WF_6 (17.0 mmol). The solid product was a mixture of a white crystalline substance and a brown powder. An attempt was made to separate them by solvent extraction but no suitable solvent could be found since both were insoluble in CS_2 , CCl_4 , Me_4Si , CCl_3F and C_6F_6 , while they both dissolved in acetone. Elemental analysis of the mixture was consistent with the 1:1.5 adduct of tungsten hexafluoride. Found, C, 17.9; H, 3.6; N, 3.7; F, 28.9; W, 45.9% $\text{WF}_6 \cdot 1.5\text{NEt}_2\text{H}$ requires C, 17.7; H, 4.0; N, 5.2; F, 28.0; W, 45.2%.

The ^1H n.m.r. spectrum of the mixture was consistent with the presence of a diethylamino compound (broad signals at 0.85 and 4.7 p.p.m. cf. WF_5NEt_2 Table 1.3). Other signals observed in ^1H n.m.r. spectrum were, a singlet at 1.55 p.p.m. assigned to solvent acetone, and a poorly resolved multiplet at 2.6 p.p.m.

Its ^{19}F n.m.r. spectrum contained one major signal (single line) at -158.9 p.p.m. assigned to WF_6 and two signals of low intensity (both single

lines) at -58.0 and -52.1 p.p.m. which were difficult to assign due to the absence of a fine structure.

Its i.r. spectrum (Nujol and fluorolube mulls) was as follows :

3150br,s, 2990m, 2945w, 2880w, 2820w, 2760w, 2480m, 2380w, 1700w, 1595s, 1465sh, 1452s, 1382s, 1375w, 1319s, 1270w, 1230w, 1185m, 1160m, 1130m, 1090m, 1065s, 1040m, 995m, 900s, 840w, 790m, 780m, 692m, 600br,s, 490w, 420w.

(b) Conductometric Titrations

The reaction of tungsten hexafluoride with diethylamine was followed by conductometric titration. Electrical conductance was measured by means of Universal conductivity bridge, model B.221. The cell used for conductometric titrations was specially adopted for vacuum use (details in Appendix). Two flasks, one containing the bright platinum disc electrodes, and the other fitted with a Teflon stop-cock were separated by a sintered glass disc. After evacuation of the flask, acetone was distilled into the cell, and its conductance noted. Tungsten hexafluoride was then introduced and the conductance of the yellow solution again noted. The measurements were made in a thermostated bath at 25°. Conductance measurements were made after various additions of Et_2NH . The solution turned brown on the addition of Et_2NH and a light green solid started precipitating when the mole ratio of Et_2NH to WF_6 approached about 1:1, and continued until it reached about 1.5-2.0. This solid was prepared later, in a separate experiment, for elemental analysis. WF_6 was reacted with four fold excess of Et_2NH in acetone. The reaction mixture was left at -60° for 24 hours and then warmed to 20°C. Liquids were transferred into a side flask and kept frozen by liquid nitrogen. The solid was then pumped on for four hours to ensure the removal of all volatiles and

finally sealed off under vacuum for analysis and infra-red spectrum.

Elemental analysis of this solid corresponded to $\text{WF}_5 \cdot \text{N}(\text{Et})_2 \cdot \text{H} \cdot \text{N}(\text{Et})_2 \cdot 0.5$ acetone. Found, C, 23.5; H, 5.5; N, 6.3; F, 21.0; W, 40.3%.

$\text{WF}_5 \cdot \text{N}(\text{Et})_2 \cdot \text{H} \cdot \text{N}(\text{Et})_2 \cdot 0.5$ acetone. Required, C, 23.9; H, 5.3; N, 6.2;

F, 21.0; W, 40.7%. The i.r. spectrum of the solid (Nujol and fluorolube mulls $4000\text{--}400\text{ cm}^{-1}$) was as follows : 3100br,w, 2900br,s, 2720w, 2400w, 1708s, 1590m, 1455s, 1375s, 1310w, 1210w, 1162m, 1150sh, 1070m, 1050sh, 955m, 945sh, 870m, 815w, 790w, 735m, 585w, 560s, 470w, 440w.

The results of the conductometric titrations are summarised in Table 1.14.

Table 1.14

Specific conductance MHO. $\times 10^{-3}$

I		II		III	
Et ₂ NH to WF ₆ mole ratio	Specific conductance MHO. 10^{-3}	Et ₂ NH to WF ₆ mole ratio	Specific conductance MHO. 10^{-3}	Et ₂ NH to WF ₆ mole ratio	Specific conductance MHO. 10^{-3}
Acetone	0.002	Acetone	0.0006	Acetone	0.0006
WF ₆ (0.673 mmol)	1.12	WF ₆ (2.7 mmol)	2.68	WF ₆ (2.23 mmol)	1.92
0.76	3.71	0.17	5.48	0.12	3.70
1.84	1.71	0.32	7.47	0.23	5.80
4.00	0.62	0.54	8.65	0.28	5.97
6.33	0.62	0.67	9.50	0.42	6.59
7.33	0.62	1.13	6.6	0.58	7.29
10.45	0.62	1.44	5.55	0.69	7.69
		1.67	4.50	0.97	5.64
		2.0	3.56	1.10	5.32
		2.28	2.61	1.32	4.69
		2.49	1.69	1.72	3.57
				2.10	2.57
				2.31	2.07
				2.58	1.39

CHAPTER TWO

THE REACTIONS OF TUNGSTEN HEXAFLUORIDE WITH SOME ORGANOSILICON
COMPOUNDS. THE PREPARATION AND PROPERTIES OF PENTAFLUORO-
PHENOXY TUNGSTEN(VI) AND MOLYBDENUM(VI) FLUORIDES

INTRODUCTION

The reactions of tungsten hexafluoride with Me_3SiX , (where X is OC_6F_5 , $\text{OC}(\text{O})\text{CH}_3$, $\text{OC}(\text{O})\text{CF}_3$, $\text{OC}(\text{O})\text{C}_3\text{F}_7$, CN and NCO), the reaction of methoxytungsten(VI)pentafluoride with trifluoroacetic anhydride, and the formation of pentafluorophenoxy molybdenum(VI)pentafluoride, are described in this chapter.

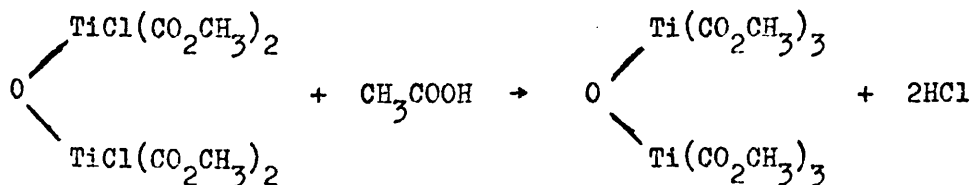
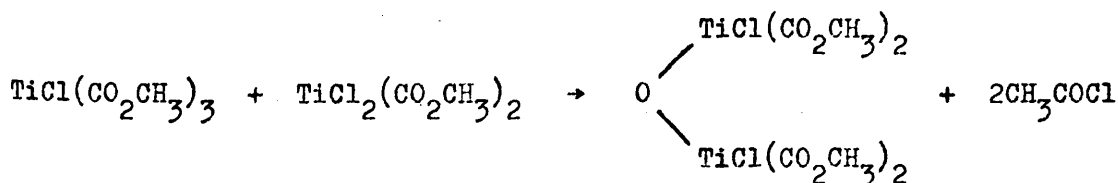
Preparations of polyfluoroaryl Grignard reagents¹⁰⁷ stimulated interest in the polyfluoroaryl derivatives, and considerable differences between phenyl and polyfluoroaryl derivatives have been found.¹⁰⁸ Although phenoxy derivatives of metal fluorides, such as tungsten hexafluoride, and non-metal fluorides, such as phosphorous pentafluoride and sulphur tetrafluoride, were well characterized, the corresponding pentafluorophenoxy compounds were not known at the time this work was started.^{43,109} A very recent report described the preparation of pentafluorophenoxy fluorides of phosphorous, $(\text{C}_6\text{F}_5\text{O})_{3-n}\text{PR}_n\text{F}_2$ ($\text{R} = \text{Me}$ or Ph ; $n = 0, 1, 2$).¹¹⁰

In the present work the preparation of pentafluorophenoxy derivatives of tungsten hexafluoride and molybdenum hexafluoride has been attempted in order to compare them with the corresponding phenoxy compounds. It has been stated that it is the electronic effects which largely determine the properties and behaviour of pentafluorophenoxy substituents.¹¹¹ The ^{19}F n.m.r. spectra of pentafluorophenoxy derivatives can provide a valuable insight into the character of the bond between tungsten and the $-\text{OC}_6\text{F}_5$

ligands.

In an attempt to correlate the n.m.r. parameters of the pentafluorophenyl group with the electronic interactions at the bond between substituent and ring, it was suggested that coupling constants among the fluorine nuclei, as well as their chemical shifts reflect changes in the ring substituent interaction. An empirical relationship between coupling constants and chemical shifts was suggested to differentiate between π donor and π acceptor substituents.¹²⁷ Application of this relationship to the pentafluorophenoxy tungsten(VI) fluorides could lead to the same information about the effect of the $-\text{OWF}_5$ group on the electron density at the ortho, meta and para, positions of the pentafluorophenyl ring. Comparisons of the n.m.r. parameters of pentafluorophenoxy tungsten(VI) fluorides with those of other $\text{C}_6\text{F}_5\text{X}$ systems were also desired

Acetic acid and acetic anhydride have been reported to react exothermally with TiCl_4 giving $\text{TiCl}_2(\text{OC}(\text{O})\text{CH}_3)_2$. Polymerisation occurred, however, when further substitution reactions were attempted yielding a mixture of basic acetates:¹¹³

$$\text{TiCl}_2(\text{CO}_2\text{CH}_3)_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{TiCl}(\text{CO}_2\text{CH}_3)_3 + \text{CH}_3\text{COCl}$$


In contrast, successive substitution reactions of acetic acid with zirconium tetrachloride led simply to the formation of zirconium tetraacetate, $\text{Zr}(\text{CH}_3\text{CO}_2)_4$. This decomposed to the basic diacetate and acetic anhydride on heating.¹¹⁴ The reaction of molybdenum pentachloride with mono-

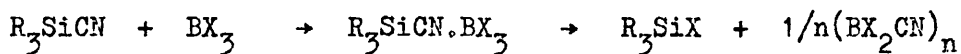
carboxylic acids or acid anhydrides in carbon tetrachloride, was reported to give molybdenum trichloride dicarboxylate, $\text{MoCl}_3(\text{RCO}_2)_2$, where $\text{R} = \text{Ph}$ or Me . The benzoate was stable thermally, but the acetate decomposed giving HCl at about 80°C .¹¹⁵

As no carboxylato derivatives of metal fluorides appear to have been reported, in this work, some attempts have been made to isolate carboxylato tungsten(VI) fluorides using the reactions of tungsten hexafluoride with $\text{Me}_3\text{SiOC}(\text{O})\text{CH}_3$ or $\text{Me}_3\text{SiOC}(\text{O})\text{R}_f$ (where $\text{R}_f = \text{CF}_3$ or C_3F_7). By this means it was hoped to compare the properties of these compounds with carboxylate derivatives of titanium, zirconium and molybdenum chlorides. Spectroscopic studies of these compounds would provide a method of investigating their stereochemistry and the metal-ligand interaction. It was also hoped to compare the behaviour of $\text{WF}_5\text{OC}(\text{O})\text{CH}_3$ and $\text{WF}_5\text{OC}(\text{O})\text{CF}_3$. The perfluoroalkyl groups are exceptional in that, despite their large size, they are of high electronegativity. For example, the CF_3 group is more electronegative than the CH_3 group, and its electronegativity is between that of chloride and fluoride. Because of this anomalous size, electronegativity ratio, they differ both from halogens as well as from corresponding alkyl groups. Compounds containing perfluoroalkyl groups are thermally more stable than the corresponding alkyl substituted compounds, and their decomposition is supposed to be by a different mechanism.¹⁰⁶ The thermal decomposition of carboxylato tungsten(VI) fluorides was thus desired for two purposes; firstly, to compare the behaviour of the two types of compounds ($\text{WF}_5\text{OC}(\text{O})\text{CH}_3$ and $\text{WF}_5\text{OC}(\text{O})\text{CF}_3$) and secondly, for the formation of organometallic compounds of tungsten of the type F_5WCH_3 and F_5WCF_3 by the elimination of CO_2 .

It has been reported that alkyl and aryl cyanides react with non-metal halides such as BX_3 ($\text{X} = \text{F}$ or Cl) to form addition compounds of the type

$\text{RCN} \cdot \text{BX}_3$ (R = Me or Ph).¹¹⁶⁻¹¹⁸ Niobium pentafluoride also forms 1:1 or 1:2 complexes with CH_3CN .^{68,118a} 1:2 Alkyl cyanide complexes of tungsten(IV) chlorides and bromides were obtained, however, from the reactions of alkyl cyanides with W(VI) and W(V) halides.¹¹⁹

In contrast to the reactions of alkyl and aryl cyanides, the reactions of R_3SiCN (assumed to be a cyanide), where R = H or Me, with the boron halides led to the formation of addition compounds which decomposed spontaneously with the elimination of silyl halides and the formation of a solid residue of general formula $(\text{BX}_2\text{CN})_n$ according to the reaction scheme:¹²⁰



Cyanato and thiocyanato derivatives of metal chlorides of the type, $\text{MCl}_n\text{X}_{5-n}$ (where M = Nb or Ta; X = CNO or CNS; n = 0-4), have been prepared by the reaction of metal chlorides with KX .^{121,122}

Since no tungsten halides with pseudo-halogen substituents are known, the reactions of R_3SiX (R = Me or Et; X = CN or NCO) with tungsten hexafluoride have been attempted with the intention of substituting CN or CNO groups for fluoride in WF_6 . The isolation of cyanotungsten(VI) fluorides would make it possible to attempt reactions on the C≡N bond, and to investigate the nature of W-ligand interactions. It was also of interest to find out if the normal oxidation state of tungsten (i.e. VI) would be retained in these reactions in view of the reduction of W(VI) and W(V) to W(IV) in the reactions of alkyl cyanides with tungsten halides.

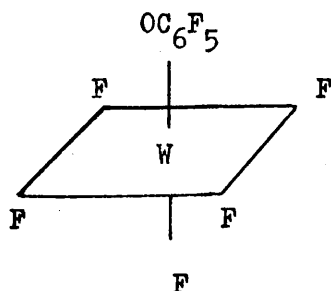
RESULTS AND DISCUSSION

REACTIONS OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLPENTAFLUORO-PHENOXYLSILANE

Formation and Spectroscopic Properties of Pentafluorophenoxytungsten(VI) pentafluoride

Tungsten hexafluoride and trimethylpentafluorophenoxyasilane, $\text{Me}_3\text{SiOC}_6\text{F}_5$, react smoothly below 20° to give Me_3SiF and a dark red liquid, which is slightly volatile at 20°C . This liquid is formulated from its analysis and spectra as pentafluorophenoxytungsten(VI)pentafluoride, $\text{WF}_5\text{OC}_6\text{F}_5$. Molecular weight determination in C_6F_6 are consistent with the monomeric nature of this compound in solution.

The ^{19}F n.m.r. spectrum of $\text{WF}_5\text{OC}_6\text{F}_5$ (Fig. 2.1.) can be interpreted on the basis of a monomeric structure, with an octahedral arrangement of ligands around tungsten, (I).



(I)

The ^{19}F n.m.r. spectral parameters of $\text{WF}_5\text{OC}_6\text{F}_5$ are summarized in Table (2.1). By comparison with the spectra of SF_5X , (Fig. 2.2), where $\text{X} = \text{Cl}$ or OPh , the spectrum of the $-\text{OWF}_5$ part of $\text{WF}_5\text{OC}_6\text{F}_5$ corresponds to an AB_4 spin system. The AB_4 peak frequencies are used to obtain δ_{AB} and J_{AB} , using analogous numbers to those previously used for SF_5X .¹²³

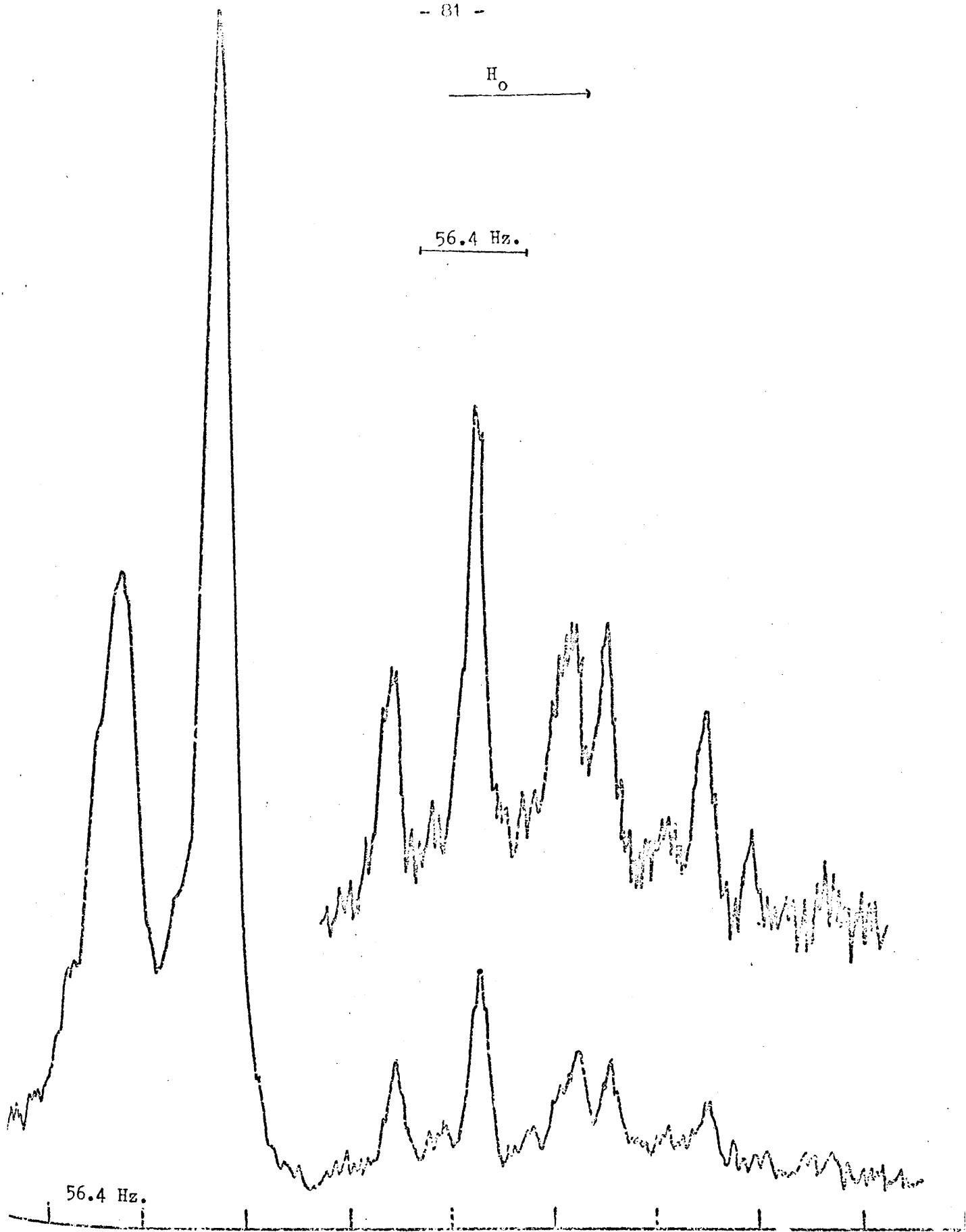


Fig. (2.1) ^{19}F n.m.r. spectrum of neat $\text{WF}_5\text{OC}_6\text{F}_5$ (spectral parameters are given in Table 2.1).

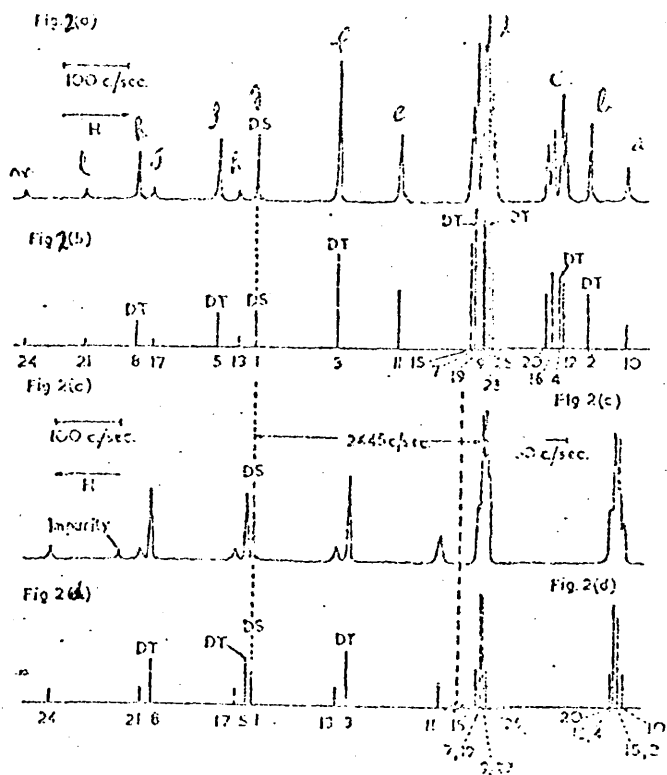


Fig. (2.2) (a) observed and (b) calculated spectrum
of $\text{SF}_5 \text{ OPh}$ (c) observed and (d) calculated
spectrum of $\text{SF}_5 \text{ Cl}$

(R.K. Harris and K.J. Packer, J.C.S. (1961), 4739)

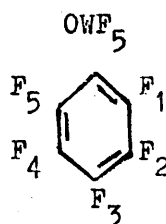
Table 2.1

¹⁹F n.m.r. parameters of WF₅OC₆F₅

Chemical Shifts (p.p.m.)	Assignments	
-145.15 (doublet)	B ₄ nuclei	J _{AB} = 69.64 Hz.
-141.28 (complex)	A nucleus	δ _{AB} = 223.03 Hz.
+150.75 (triplet)	para fluorine of C ₆ F ₅	$\frac{J_{AB}}{\delta_{AB}} = 0.312$
+151.76 (br. doublet)	ortho fluorines of C ₆ F ₅	J ₂₃ = J ₃₄ = 19.8 Hz. ^a
+160.48 (br. triplet)	meta fluorines of C ₆ F ₅	J ₅₄ + J ₅₂ = J ₁₂ + J ₁₄ = 18.0 Hz. ^a

^a The signs for the coupling constants are not known. Numbering is clockwise around the ring with the ortho-fluorines at 1 and 5.

The appropriate equations are :-



$$\delta_{AB} = E_1 - E_7 + \frac{1}{2}(E_7 - E_4)$$

$$3(J_{AB}) = 2(E_8 - E_3) - (E_7 - E_4)$$

where E_i is the position in Hz of the ith line relative to CCl₃F.

Assignments for the spectrum due to the pentafluorophenyl part of WF₅OC₆F₅ (Fig. 2.3) are made by comparison with the spectrum of C₆F₅Cl, (A₂B₂X system).¹²⁴

The comparison between ¹⁹F chemical shifts of the -OWF₅ group of WF₅OC₆F₅ with corresponding chemical shifts of various WF₅X (where X = NEt₂, Cl, OPh, OMe) compounds (Table 2.2) indicates the fairly strong electronegative character of the -OC₆F₅ group in WF₅OC₆F₅.

$\xrightarrow{\text{H}_2\text{O}}$

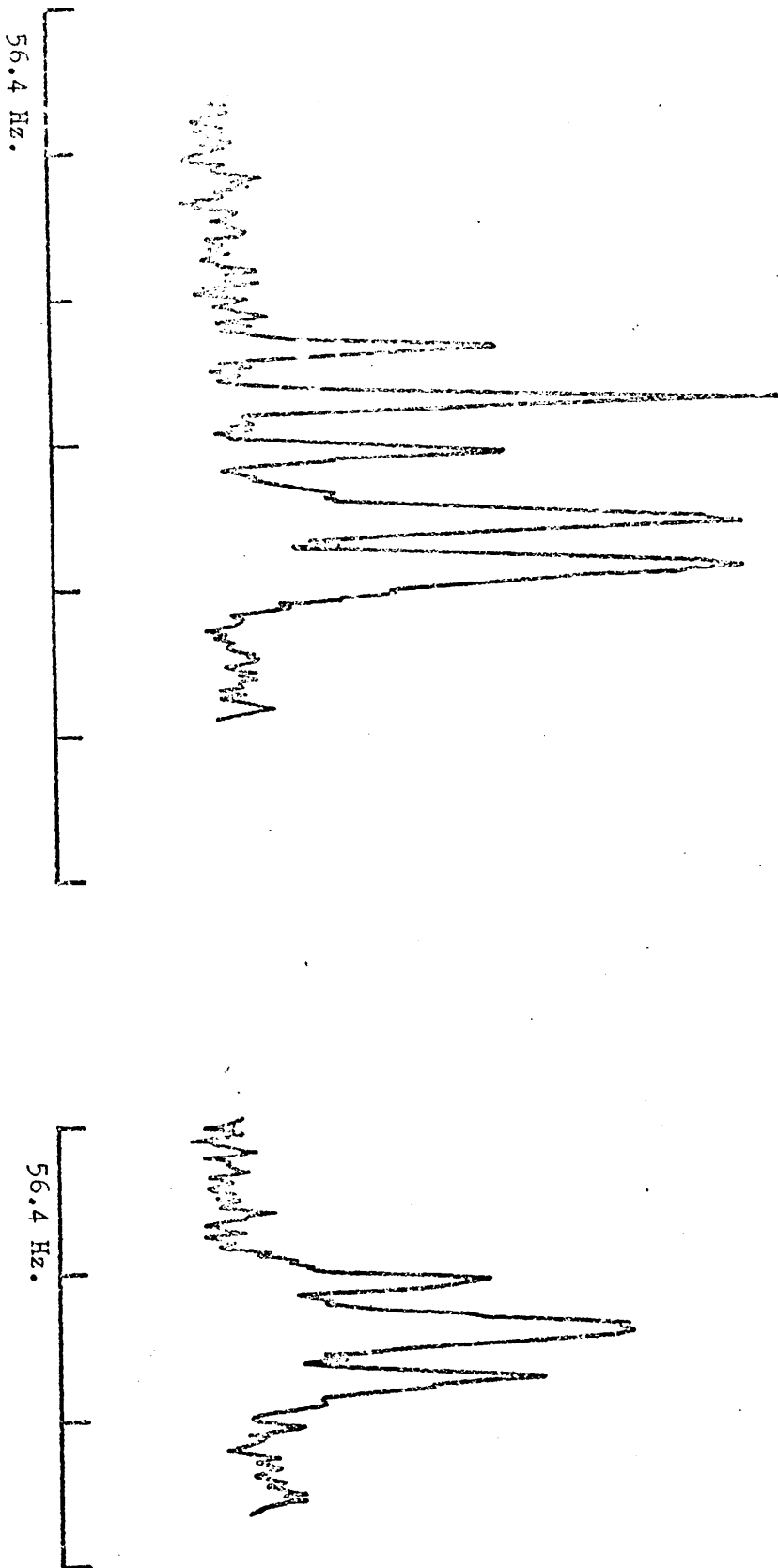


Fig. (2.3) ^{19}F n.m.r. spectrum due to C_6F_5 part of $\text{WF}_5\text{OC}_6\text{F}_5$ (spectral parameters are given in Table (2.1)).

Table 2.2

Compound	Chemical Shifts		$\delta[F(1) - F(2)]^b$ (p.p.m.)	Ref.
	(p.p.m.)			
	F(1) ^a	F(2) ^a		
WF ₅ OC ₆ F ₅	-145.2	-141.3	3.9	
WF ₅ Cl	-182.0	-126.5	55.0	50
WF ₅ OPh	-126.5	-112.0	14.5	43
WF ₅ NEt ₂		-126.0		86
WF ₅ OMe	-118.5	-89.5	29.0	43

^a F(1) trans to F, F(2) trans to X (X = OC₆F₅, Cl, OPh, NEt₂, OMe).

^b Chemical shift difference between F(1) and F(2) in p.p.m.

Although the fluorine trans to the substituent is still shielded more than the fluorine trans to fluorine, $\delta[F(1) - F(2)]$ is a minimum in WF₅OC₆F₅ and increases in the order WF₅OC₆F₅ < WF₅OPh < WF₅OMe < WF₅Cl. The relative deshielding of the fluorines in WF₅OC₆F₅ compared with other WF₅X compounds may be explained in terms of a combination of steric and inductive effects.

The chemical shifts of the phenyl group are believed to be a measure of the electron density at the nucleus.¹²⁶ Substituent effects on the electronic distribution can therefore be inferred by the chemical shifts of nuclei at different positions in the benzene ring. Thus it has been found that the ortho fluorine shift is influenced by a combination of inductive, steric and resonance effects, the meta shifts mainly by inductive effects and the para fluorine shift mainly by resonance effects.^{125, 126} Moreover para ¹⁹F chemical shifts have been shown to be more sensitive to

resonance interaction than ortho ^{19}F chemical shifts.^{122a, 125} Thus ^{19}F chemical shifts for para fluorine in pentafluorophenyl derivatives has been suggested as a possible probe for indicating $d_{\pi} - p_{\pi}$ interaction between C_6F_5 and substituents. Relatively large para shifts to low field means greater $d_{\pi} - p_{\pi}$ interaction in the pentafluorophenyl derivatives.¹⁰⁸

The ortho, meta and para fluorine chemical shifts of the C_6F_5 group in $\text{WF}_5\text{OC}_6\text{F}_5$ are at a lower field than the corresponding shifts in $\text{Me}_3\text{SiOC}_6\text{F}_5$. The relative difference of the ortho and meta chemical shifts (7.0 and 5.1 p.p.m. respectively) in the two compounds are small compared with the difference in para chemical shift (17.7 p.p.m.). $\text{WF}_5\text{OC}_6\text{F}_5$ appears to be a unique example among pentafluorophenoxy derivatives in two respects. Firstly, the para chemical shift is at a lower field than the ortho and meta fluorine chemical shifts. Secondly, the difference between ortho and para fluorine chemical shifts is smallest (1.01 p.p.m.) of any ortho-para shifts observed. The relatively large para shift to low field which is observed for $\text{WF}_5\text{OC}_6\text{F}_5$ indicates that $\text{O} \rightarrow \text{W } p_{\pi} \rightarrow d_{\pi}$ interaction is significant in this compound.

Generally, with the decreasing electronegativity and increasing size of the substituent X in pentafluorophenyl derivatives, $\text{C}_6\text{F}_5\text{X}$, the ortho fluorines move to a far lower field than para fluorine.¹²⁵ The difference between the ortho and para fluorine chemical shifts, δ_{OP} , is small however, in compounds where resonance effects are more significant. Comparison of δ_{OP} in some pentafluorophenyl derivatives (Table 2.3), suggests that resonance effects dominate in $\text{WF}_5\text{OC}_6\text{F}_5$ over the inductive and steric effects of the $-\text{OWF}_5$ group.

Recently, Graham et al^{126, 127} have investigated the ^{19}F n.m.r. spectra of a large number of pentafluorophenyl derivatives. They have found a linear relationship between J_{OP} , the coupling constant between the ortho and para

Table 2.3

Compound	δ_{OP}^a (p.p.m.)	Ref.
$C_6F_5O^+WF_5$	1.7	
C_6F_5OMe	-6.0	125
C_6F_5OH	-6.8	125
$C_6F_5CF_3$	-7.6	126
$C_6F_5OSiMe_3$	-8.9	126
C_6F_5CN	-11.2	126
$C_6F_5SnMe_3$	-30.5	125
C_6F_5HgMe	-31.6	125
$C_6F_5SnPh_3$	-33.3	126
C_6F_5I	-33.5	125

^a = Difference between ortho and para fluorine chemical shifts.

fluorine atoms of the pentafluorophenyl group, and δ_p the chemical shift of the para fluorine. They suggest that the straight line relationship, $J_{OP} - \delta_p$ distinguishes between π electron donation to the ring and π electron withdrawal from the ring by the substituent group. Thus substituents giving the low δ_p and the high J_{OP} (e.g. -CN) are considered strong π electron acceptors, while the substituents giving high δ_p and high J_{OP} (e.g. -NH₂) are regarded as π donors. Intermediate δ_p and low J_{OP} values imply a weak π interaction (e.g. -CH₃).

The doublet assigned to ortho fluorines and the triplet assigned to meta fluorines, in the spectrum due to pentafluorophenyl part of $WF_5OC_6F_5$,

are broad. By analogy with the spectrum of C_6F_5Cl these signals are expected to split further. However, due to the lack of fine structure in the present case, complete analysis of the spectrum is not possible. Thus accurate values for J_{OP} are not known for $WF_5OC_6F_5$. Appropriate values can however be calculated using general equation relating J_{OP} with δ_m and δ_p , the chemical shifts of meta and para fluorines respectively. These relations were established by Graham et al;¹²⁷ and were found to be applicable to all the 61 pentafluorophenyl derivatives investigated by them. The appropriate equations are:

$$J_{OP} = -0.453 \delta_p + 71.98$$

$$J_{OP} = -1.47 \delta_m + 239.3$$

$$J_{OP} = -0.524 \delta_p + 0.262 \delta_m + 40.69$$

The values of J_{OP} for $WF_5OC_6F_5$ calculated from above equations are 3.7, 3.4 and 3.7 Hz. respectively. The average value is 3.6 Hz.

Following the approximate value of J_{OP} for $WF_5OC_6F_5$, it can be compared with the corresponding values for some other pentafluorophenyl derivatives (Table 2.4). It is not reasonable to draw any definite conclusion from such comparison since J_{OP} is chemical shift dependent and not the experimental value as for other compounds. However, the value of J_{OP} calculated is consistent with the previous finding; that the $-OWF_5$ group is a π electron acceptor group.

Tentative assignments for the infra-red and Raman spectra of $WF_5OC_6F_5$ are listed in Table (2.5). The assignments for C-F and aromatic absorptions have been made by comparison with C_6F_6 ,¹²⁹ C_6F_5X (where $X = Cl, Br, I$)¹³⁰ and some other pentafluorophenyl derivatives.¹³¹ Metal-O-C stretches in $Et_4N[W(OR)]Cl_5$ ($R = Me, Et, Pr$),¹³² $W_2(OEt_2)_2 \cdot (EtOH)_4 \cdot Cl_4$ ¹³³ and metal alkoxides of the formula $M(OR)_4$ ($M = Ti, Zr, Hf, Ge, Al, Si$; $R = Me,$

Table 2.4

Compound	δ_P (p.p.m.)	J_{OP} (Hz.)	Ref.
$C_6F_5OF_5$	150.0	3.6	
$C_6F_5PF_2$	147.4	5.9	128
C_6F_5CN	143.2	5.8	126
$C_6F_5CF_3$	147.8	5.8	126
$C_6F_5CO_2H$	151.6	4.0	126
$C_6F_5P(NMe_2)_2$	155.7	2.6	126
C_6F_5I	153.0	2.0	125
C_6F_5H	154.3	1.3	126
C_6F_5Br	155.2	1.1	126
C_6F_5Cl	156.5	0.7	125
$C_6F_5CH_3$	159.1	0.0	126
$C_6F_5OSiMe_3$	167.6	-4.4	126
$C_6F_5OGepPh_3$	169.2	-5.0	126
C_6F_5OH	171.2	-6.1	125
$C_6F_5NHSiMe_3$	174.1	-7.0	126

Table 2.5

Infra-red and Raman spectra of pentafluorophenoxytungsten(VI)pentafluoride.

Infra-red (Liquid)	Raman (Liquid)	Assignment	Ref.
1642 m	1633 s		
1530 s		Ring Stretch	129-131
1515 s			
1470 sh	1472 v.s.		
1365 m		$\nu(\text{C-F})\text{Sym}$	
1332 s	1332 s		
1260 w		Ring Stretch	
1192 s	1198 v.s.	$\nu(\text{C-F})\text{Antisym}$	
1050 s	1051 s	$\nu(\text{C-F})\text{Sym}$ }	129-135
1001 s		$\nu(\text{W-O-C})$ }	
	767 s		
722 s	724 w	$\nu(\text{W-F})$	51,86a
670 s		$\delta(\text{C-F})\text{Antisym}$ }	51,86a
		$\nu(\text{W-O})$ }	129-135
		$\nu(\text{W-F})\text{Asym}$ }	
502 w	498 m	Ring Stretch	129-131
455 w		Antisym Ring deformation	
	285 w	$\delta(\text{C-F})\text{Sym}$ }	129-131
		$\delta(\text{W-F})$ }	51,86a
		Ring angle deformation }	

Et),^{134,135} have been assigned in the region $(967-1155)\text{cm}^{-1}$. The choice for W-O-C in $\text{WF}_5\text{OC}_6\text{F}_5$ appears to be 1051 or 1001 cm^{-1} in the infra-red and 1051 in the Raman. Since $\nu(\text{C-F})$ is also expected in this region,¹²⁹⁻¹³¹ distinction between the two absorptions is not possible. $\nu(\text{W-F})$ at 767 and 724 cm^{-1} in the Raman and 722 cm^{-1} in the infra-red is assigned by comparison with WF_5Cl ⁵¹ and WF_6 .^{86a} Definite assignments for the bands at 670 cm^{-1} in the infra-red and 285 cm^{-1} in the Raman are difficult due to the possibility of many absorptions in this region (see Table 2.5).

The colour of $\text{WF}_5\text{OC}_6\text{F}_5$ is due to the presence of an intense electronic absorption in the near U.V. region which tails into the visible region (ν_{max} . Table 2.6). The electronic spectrum of $\text{WF}_5\text{OC}_6\text{F}_5$ is similar to that of WF_5OPh . Both spectra are solvent independent, and have broad band in approximately the same region. By analogy with the spectrum of WF_5OPh , the electronic absorptions in WF_5OPh are assigned to intramolecular charge transfer between the π system of the pentafluorophenyl group, and the non bonding orbitals of tungsten.

Table 2.6

Electronic spectra of $\text{WF}_5\text{OC}_6\text{F}_5$ and other substituted derivatives of tungsten hexafluoride

Compound	Solvent	$\nu_{\text{max.}} \times 10^{-3}\text{ cm}^{-1}$	Ref.
WF_5Cl	Gas	37.0	49
WF_5NEt_2	Me_4Si	36.5	86
$\text{W}(\text{NMe}_2)_6$	(toluene ?)	(30.0-33.0)	61
WF_5OPh	C_6F_6 or Me_4Si	27.8	47
$\text{WF}_5\text{OC}_6\text{F}_5$	C_6F_6	28.60	
	Me_4Si	29.0	

REACTION OF TUNGSTEN HEXAFLUORIDE (1MOLE) WITH TRIMETHYLPENTA-
FLUOROPHENOXYSIANE (2 MOLES)

The reaction of tungsten hexafluoride with trimethylpentafluorophenoxy-
silane (1:2 mole ratio) occurs smoothly at 20° giving Me_3SiF , and
a red liquid, which is slightly volatile at 20°C. The red liquid
analyses to bis(pentafluorophenoxy)tungsten(VI)tetrafluoride, $\text{WF}_4(\text{OC}_6\text{F}_5)_2$.
The ^{19}F n.m.r. spectrum of this liquid (Fig. 2.4 - 2.6), however, indicates the
presence of more than one species. Assignments for the ^{19}F spectrum are
summarized in Table (2.7).

The signals at -144.0 (doublet) and -137.5 p.p.m. (multiplet) are
assigned to $\text{WF}_5\text{OC}_6\text{F}_5$ by comparison with the spectrum of pure $\text{WF}_5\text{OC}_6\text{F}_5$
(Fig. 2.1). The symmetrical multiplet of 14 at -123.1 p.p.m. is characteristic
of an A_2B_2 type spectrum (Fig. 2.5). It is thus assigned to cis
 $\text{WF}_4(\text{OC}_6\text{F}_5)_2$. Since fluorines trans to fluorines are expected at a lower
field than the fluorines trans to some other substituent, the singlet at
-132.2 p.p.m. is assigned to trans- $\text{WF}_4(\text{OC}_6\text{F}_5)_2$. The weak doublet at
-113.5 p.p.m. is assigned to trans- $\text{WF}_3(\text{OC}_6\text{F}_5)_3$ with the assumption that
either the triplet expected for the axial fluorine is too weak to be
observed or is masked by the singlet at -105.3 p.p.m. Assignments for
the singlets in n.m.r. spectra are never satisfactory, Hence, only tentative
assignments are made for the singlets at -132.2, -105.3 and -68.9 p.p.m.
The spectrum due to C_6F_5 groups (Fig. 2.6) is too complex to make any
unambiguous assignments. However, it indicates the presence of more than
one species.

Dean and Evans,¹³⁶ have shown that ^{19}F chemical shifts, relative to
 SnF_6^{-2} , in substituted hexafluorostanates may be represented by $\delta(\text{F}) =$
 $p\text{C} + q\text{T}$, where C and T are constants characteristic of a substituent, and
p and q are the numbers of substituents cis and trans respectively, to the

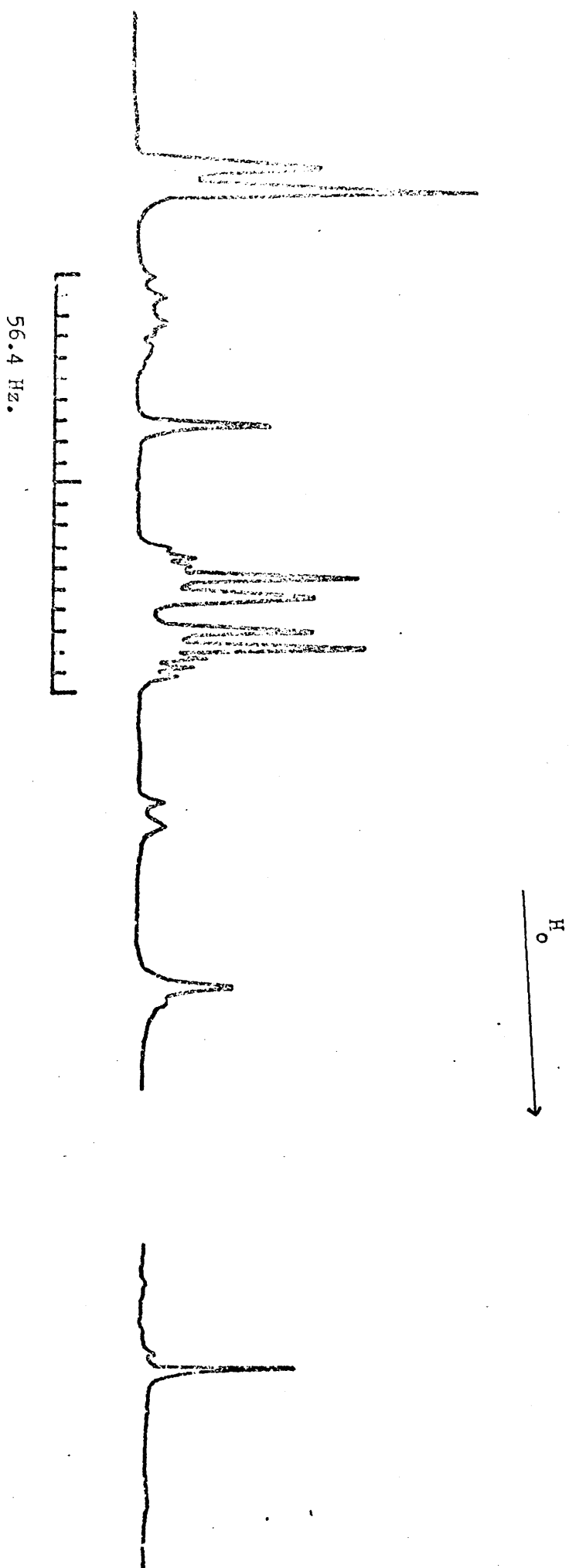


Fig. (2.4) The ^{19}F n.m.r. spectrum of red liquid obtained from the reaction of tungsten hexafluoride (1 mole) with trimethylpentafluorophenoxysilane (2 moles). Spectral parameters are given in Table (2.7)

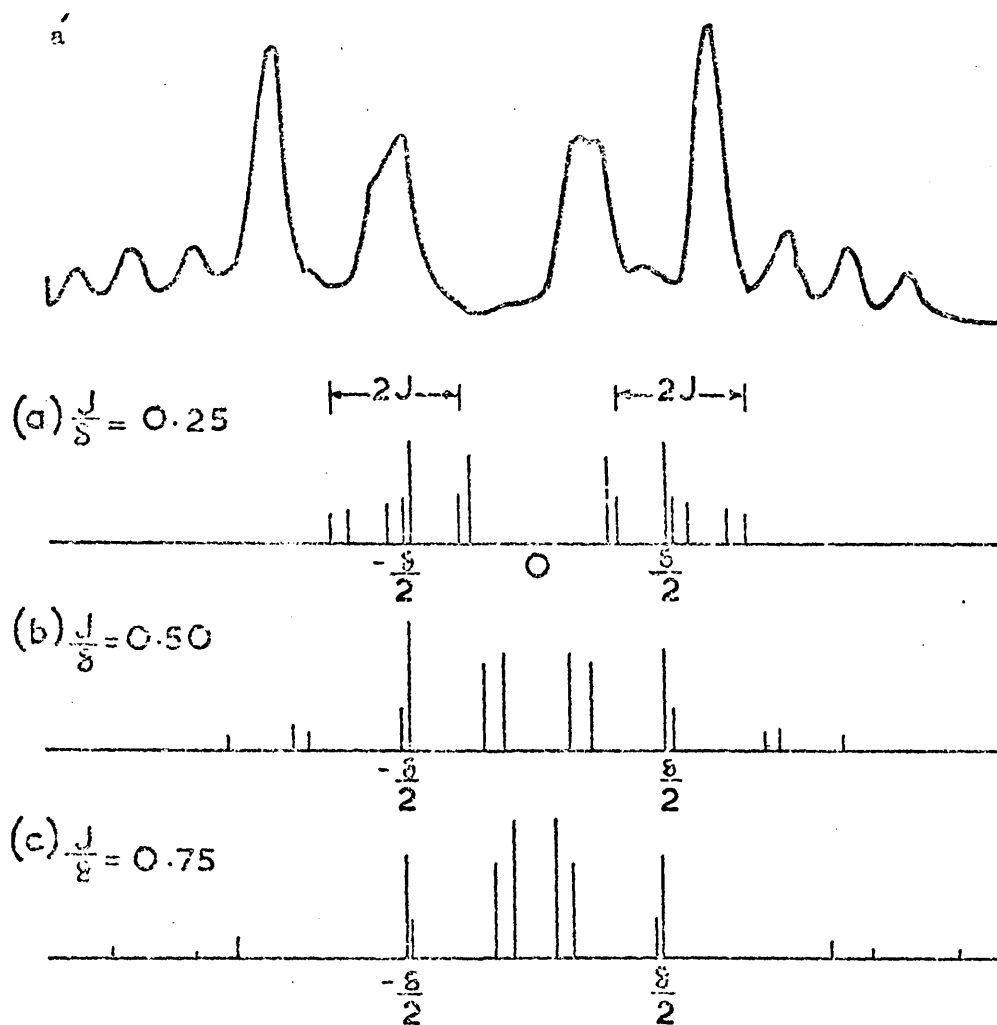


Fig. (2.5) (a') observed spectrum of cis $\text{WF}_4(\text{OC}_6\text{F}_5)_2$.

a, b and c: calculated spectrum of A_2B_2 system (P.L. Corio, Chem. Rev. (1960), 395).

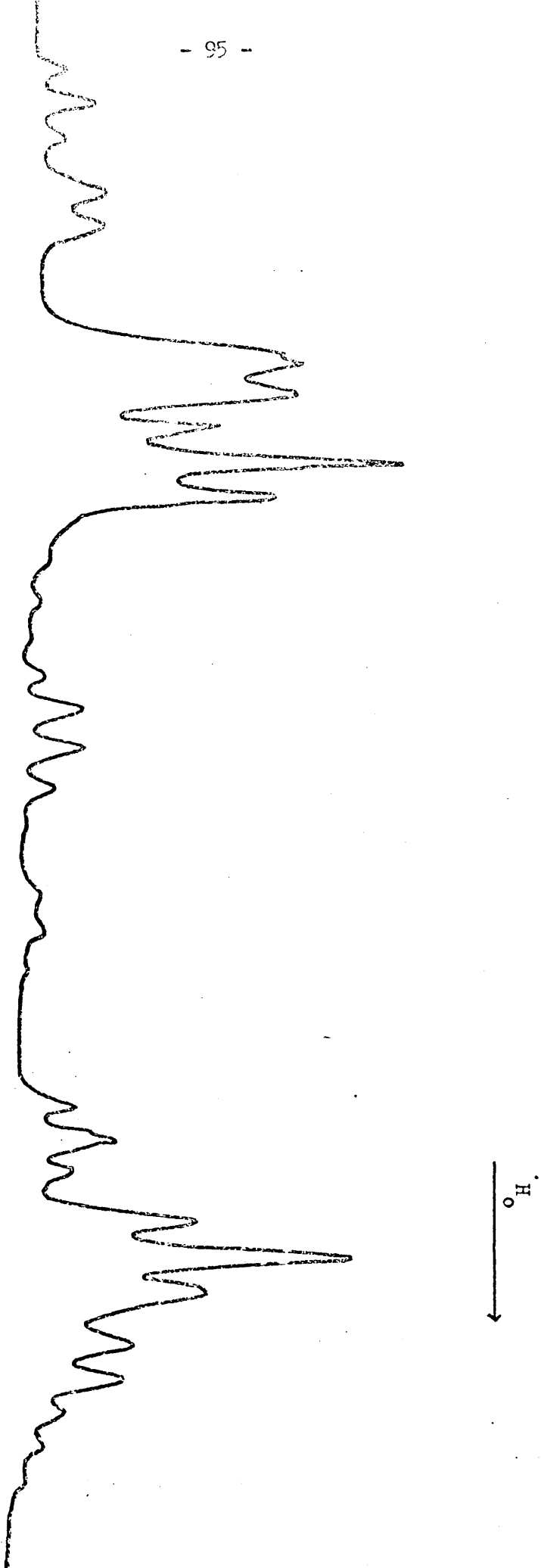


Fig. (2.6) The ^{19}F spectrum due to $-\text{C}_6\text{F}_5$ for the product from the reaction of tungsten hexafluoride (1 mole) with $\text{Me}_3\text{SiOC}_6\text{F}_5$ (2 moles).

Table 2.7

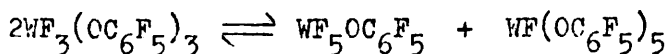
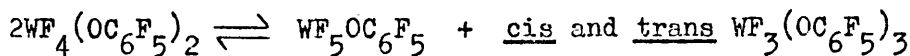
Chemical Shifts p.p.m.	Assignments
-144.0 (doublet)	$\text{WF}_5\text{OC}_6\text{F}_5(\text{B}_4)$
-137.5 (multiplet)	$\text{WF}_5\text{OC}_6\text{F}_5(\text{A})$
-132.2 (singlet)	<u>trans</u> - $\text{WF}_4(\text{OC}_6\text{F}_5)_2^t$
-123.1 (symmetrical multiplet of 14)	<u>cis</u> - $\text{WF}_4(\text{OC}_6\text{F}_5)_2$ $J = 64.8 \text{ Hz}; J/\nu_0 = 0.35$
-113.5 (doublet)	<u>trans</u> - $\text{WF}_3(\text{OC}_6\text{F}_5)_3$ $J_{F-F} = 59 \text{ Hz}$
-105.3 (singlet)	<u>cis</u> - $\text{WF}_3(\text{OC}_6\text{F}_5)_3^t$
-68.9 (singlet)	$\text{WF}(\text{OC}_6\text{F}_5)_5^t$
156.3 (triplet)	<u>para</u> -fluorine of C_6F_5 in $\text{WF}_5\text{OC}_6\text{F}_5^t$
157.3 (broad doublet)	<u>ortho</u> -fluorines of C_6F_5 in $\text{WF}_5\text{OC}_6\text{F}_5^t$
166.3 (broad triplet)	<u>meta</u> -fluorines of C_6F_5 in $\text{WF}_5\text{OC}_6\text{F}_5^t$
158.8 (br. doublet)	<u>ortho</u> -fluorines of C_6F_5 in <u>cis</u> and <u>trans</u> $\text{WF}_4(\text{OC}_6\text{F}_5)_2^t$
159.8 (multiplet of three)	<u>para</u> -fluorine of C_6F_5 in <u>cis</u> and <u>trans</u> $\text{WF}_4(\text{OC}_6\text{F}_5)_2^t$
167.5 (br. triplet)	<u>meta</u> -fluorines of C_6F_5 in <u>cis</u> and <u>trans</u> $\text{WF}_4(\text{OC}_6\text{F}_5)_2^t$
162.3 (multiplet)	?]
164.3 (br. complex)	
169.3 (complex multiplet)	

t = tentative assignments

^{19}F nucleus. The chemical shifts in $\text{WF}_{6-n}(\text{OC}_6\text{F}_5)_n$ may be similarly represented if $C = 18$ and $T = 24$. The experimental and calculated shifts relative to WF_6 are shown in Table (2.8). The assignment of the singlets at -132.2 , -105.3 and -68.9 p.p.m. (relative to CCl_3F) are based on these calculations. The agreement is by no means perfect but average difference between the calculated and experimental values (2.3 p.p.m.) is not large and thus supports the assignments made.

The infra-red spectrum of this liquid differs from that of $\text{WF}_5\text{OC}_6\text{F}_5$ in the $1200-660\text{ cm}^{-1}$ region. In addition to the absorption due to $\text{WF}_5\text{OC}_6\text{F}_5$ (Table 2.5), there are additional bands at 920 w , 785 w , and 690 v.s. cm^{-1} . The strong bands at 1192 , 1050 , 1001 and 670 cm^{-1} in $\text{WF}_5\text{OC}_6\text{F}_5$ are shifted to 1169 , 1035 , 999 and 660 cm^{-1} (all very strong) in this case. The assignments are the same as for $\text{WF}_5\text{OC}_6\text{F}_5$ and are listed in Table (2.9).

Unlike $\text{WF}_4(\text{OR})_2$ ($R = \text{Me}$ or Ph),⁴³ $\text{WF}_4(\text{OC}_6\text{F}_5)_2$ exists in both cis and trans forms. It thus resembles WF_4Cl_2 .⁵⁰ The mechanism of the reaction of WF_6 (1 mole) with $\text{Me}_3\text{SiOC}_6\text{F}_5$ (2 moles) is not known. However it appears that cis and trans $\text{WF}_4(\text{OC}_6\text{F}_5)_2$ initially formed undergo redistribution reactions as does WF_4Cl_2 ⁵⁰ to give other members of the series, $\text{WF}_{6-n}(\text{OC}_6\text{F}_5)_n$. The following scheme is proposed for redistribution reactions :



REACTION OF MOLYBDENUM HEXAFLUORIDE WITH TRIMETHYLPENTAFLUORO-PHENOXY-SILANE

Molybdenum hexafluoride reacts smoothly at -60° with $\text{Me}_3\text{SiOC}_6\text{F}_5$ giving

Table 2.8

Comparison of the experimental and calculated ^{19}F chemical shifts.

Compound	Experimental		Calculated	
	Chemical Shifts		Chemical Shifts	
	(p.p.m.) ^a		(p.p.m.) ^b	
	F(1) ^c	F(2) ^c	F(1) ^c	F(2) ^c
$\text{WF}_5\text{OC}_6\text{F}_5$	21	28	18	24
<u>trans</u> - $\text{WF}_4(\text{OC}_6\text{F}_5)_2$	33		36	
<u>cis</u> - $\text{WF}_4(\text{OC}_6\text{F}_5)_2$	40	44	36	42
<u>trans</u> - $\text{WF}_3(\text{OC}_6\text{F}_5)_3$	52	?	54	59
<u>cis</u> - $\text{WF}_3(\text{OC}_6\text{F}_5)_3$		60		60
$\text{WF}(\text{OC}_6\text{F}_5)_5$		96		96

^a from WF_6 , calculated from the relation, $\delta(\text{WF}_6) =$

$\delta(\text{CCl}_3\text{F}) + 165$ p.p.m; ^b calculated from $\delta(\text{F}) = 18p + 24q;$

^c F(1) trans to F, F(2) trans to OC_6F_5 with monomeric structures assumed.

Table 2.9

Infra-red spectrum of the red liquid obtained from the
reaction of WF_6 (1 mole) with $\text{Me}_3\text{SiOC}_6\text{F}_5$ (2 moles)

1642 m]	ring stretch
1530 sh		
1512 v.s.]		

1365 m]	$\nu(\text{C-F})$ Sym.
1335 s		
1169 s		

1035 v.s.]]	$\nu(\text{C-F})$ Sym.]
999 v.s.]		
920 w		

785 w]	$\nu(\text{W-F})$
722 s		

690 v.s.]]	$\nu(\text{C-F})$ Antisym.]
660 v.s.]		

505 w	ring stretch
-------	--------------

455 w	ring angle deformation
-------	------------------------

Table 2.10

The infra-red spectrum of $\text{MoF}_5\text{OC}_6\text{F}_5$

1640 m]	ring stretch
1515 s		
1410 s		$\nu(\text{C-F})\text{Sym.}$
1325 w]	$\nu(\text{C-F})\text{Antisym.}$
1265 w		
1225 w		
1190 w		
1169 w		
1035 m]	$\nu(\text{C-F})\text{Sym.}$
1001 s		$\nu(\text{Mo-O-C})$
800 w]	$\nu(\text{Mo-F})$
767 w		
735 w		
725 w		
675 m]	$\nu(\text{C-F})\text{Antisym.}$
635 m		
620 s		$\nu(\text{Mo-O})$
589 w		$\nu(\text{Mo-F})\text{Asym.}$
460 w		ring angle deformation

metallic dark green crystals, which are soluble in C_6F_6 , Me_4Si and C_6H_6 giving orange solutions. These crystals are involatile at 20° and hydrolyse readily in moist air. The crystalline solid is formulated from its analysis and infra-red spectrum as, pentafluorophenoxymolybdenum(VI)-pentafluoride $MoF_5OC_6F_5$.

The infra-red spectrum of $MoF_5OC_6F_5$ is similar to that of $WF_5OC_6F_5$ (Table 2.10), but no n.m.r. spectrum could be obtained in C_6F_6 . There appear to be two possible reasons for the absence of n.m.r. signals. Firstly, reduction of Mo(VI) to Mo(V) which is paramagnetic, can cause larger line broadening, to the extent that no spectrum can be observed. Secondly, the rapid fluorine exchange can also result in line broadening. Oxidation titrations will have to be carried out to decide about the first possibility and low temperature studies are required to prove the second possibility.

The electronic spectrum of $MoF_5OC_6F_5$ in Me_4Si shows a broad band at $19.4 \times 10^3 \text{ cm}^{-1}$ ($18.9 \times 10^3 \text{ cm}^{-1}$ in C_6F_6). This band occurs at a longer wavelength than the corresponding band for $WF_5OC_6F_5$. This is consistent with the stronger oxidising power of Mo(VI) in comparison with W(VI).

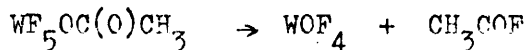
REACTIONS OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLSILYLACETATE

Tungsten hexafluoride reacts smoothly with trimethylsilylacetate, $Me_3SiOC(O)CH_3$, at -80° giving Me_3SiF , $MeCOF$, and a viscous orange liquid. The orange mass shows a band at 1790 cm^{-1} in the infra-red spectrum characteristic of a carbonyl group,^{85a} and gives off CO_2 and $MeCOF$ at 20° , the rate of evolution of CO_2 and $MeCOF$ increasing with temperature. The analysis of the compound indicates the presence of more than one species.

These results suggest that the reaction is more complex than the expected substitution reaction :



It is proposed that $\text{WF}_5\text{OC(O)CH}_3$ forms initially, but is thermally unstable, decomposing according to the reaction :



and as the temperature increases, a secondary decomposition reaction becomes possible.



Unfortunately this scheme is based only on the identification of the volatiles, for the solid products could not be characterized. However, the presence of a strong band at 1025 cm^{-1} in the infra-red spectrum of the solids favours the presence of W=O species.⁸⁷

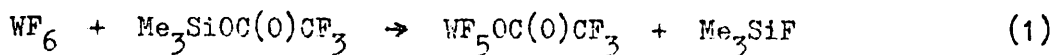
Unusually large amounts of SiF_4 were detected in these reactions. So it is also likely that some fluorination of the methyl groups of $\text{Me}_3\text{SiOC(O)CH}_3$ takes place during the course of these reactions. The decomposition of WF_5CH_3 , proposed as one of the decomposition products of these reactions, can also result in large amounts of SiF_4 .

REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLSILYLTRI- FLUOROACETATE

The reaction of WF_6 with $\text{Me}_3\text{SiOC(O)CF}_3$ differs from its reaction with $\text{Me}_3\text{SiOC(O)CH}_3$ in that trifluoro acetic anhydride, $(\text{CF}_3\text{CO})_2\text{O}$, rather than trifluoro acetyl fluoride, CF_3COF , forms. The other products of this reaction include Me_3SiF , SiF_4 (trace) and a white crystalline material mixed with trace amounts of a brown substance. Elemental analysis of the solid corresponds to oxotetrafluoro tungsten(VI),

WF₆, but the n.m.r. spectrum in C₆F₆ solution, in which it is sparingly soluble, is consistent with the presence of more than one species.

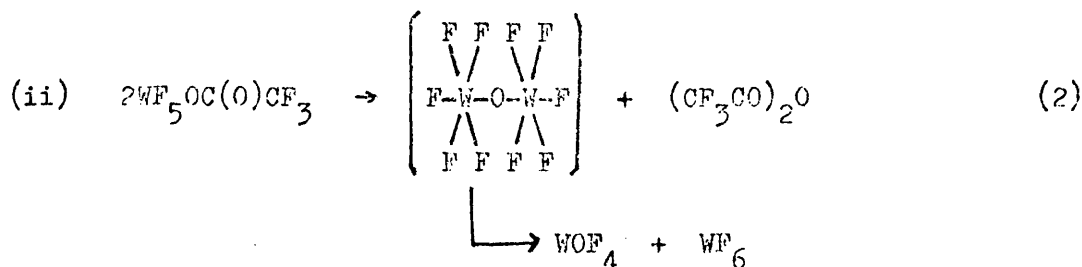
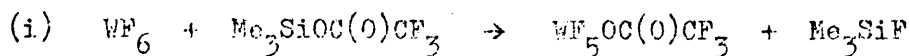
The quantity of the volatiles recovered is greater than that expected from reaction (I) (see Table 2.11)



It is very difficult to account for the excess, particularly as no unreacted Me₃SiOC(O)CF₃ and volatile tungsten containing species other than WF₆ are detected. It appears that WF₅OC(O)CF₃ initially forms but being unstable decomposes. The decomposition of WF₅OC(O)CF₃ is however different from that of WF₅OC(O)CH₃. The following reaction scheme is consistent with the observations made.

Table 2.11

Reactants (mmol)	Weight of the volatiles			
	Found (gms)	Expected		
		Reaction Scheme		Reaction Scheme
		(1)	(gms)	(2) (gms)
WF ₆ (12.1) + Me ₃ SiOC(O)CF ₃ (7.44)	4.2	2.1		4.0
WF ₆ (9.26) + Me ₃ SiOC(O)CF ₃ (2.73)	3.0	2.2		3.0
WF ₆ (10.3) + Me ₃ SiOC(O)CF ₃ (10.4)	4.0	1.0		3.6



The reaction of WF_6 with $\text{Me}_3\text{SiOC(O)C}_3\text{F}_7$ is too slow to isolate any products other than a trace amount of an orange powder and some Me_3SiF . The powder could not be characterized.

REACTION OF METHOXYTUNGSTEN(VI)PENTAFLUORIDE WITH TRIFLUOROACETIC ANHYDRIDE

WF_5OMe dissolves in $(\text{CF}_3\text{CO})_2\text{O}$ giving a yellow solution which darkens on heating. The n.m.r. spectrum of the solution, both before and after heating, is very complicated, and though the absence of fine structure precludes any definite conclusions, it suggests a much more complex reaction.

REACTIONS OF TRIALKYLSILYL CYANIDES WITH TUNGSTEN HEXAFLUORIDE

Reactions of WF_6 with R_3SiCN ($\text{R} = \text{Et}$ or Me) yield Me_3SiF and a black, fluffy powder insoluble in CCl_4 , CHCl_3 , CH_3CN , CH_3NO_2 , CCl_3F , Me_4Si , acetone, benzene, hexafluorobenzene, toluene, and hexane. Analysis of the solid corresponds to $\text{WF}_2(\text{CN})_3\text{RCN}$ ($\text{R} = \text{Me}_3\text{Et}_3$). The presence of a medium band at 2150 cm^{-1} in the infra-red spectrum of this compound is consistent with the presence of a cyanide group.^{85a} Hydrolysis of the product leads to the formation of HCN and an unidentified compound whose i.r. spectrum contains a strong band, at 1745 cm^{-1} characteristic of a carbonyl group.^{85a}

The evidence presented above suggests that some substitution has occurred in these reactions of WF_6 with R_3SiCN , but products obtained are not pure. Some further work, such as X-ray analysis, and search for a suitable solvent for n.m.r. studies, appears necessary for the characterization of these compounds.

REACTION OF TRIMETHYLSILYL ISOCYANATE WITH TUNGSTEN HEXAFLUORIDE

The reaction of WF_6 with Me_3SiNCO at 20°C gives Me_3SiF and an orange solid. The orange solid is insoluble in CCl_4 , CHCl_3 , CH_3CN , CH_3NO_2 , CCl_3F , Me_4Si , acetone, benzene, toluene, hexane and C_6F_6 . The analysis of the solid suggests the presence of more than one species. Its infrared spectrum contains a broad band at 2180 cm^{-1} which can be assigned to the $-\text{NCO}$ group.^{85a}

The results described above lead to similar conclusion as drawn for the reaction of WF_6 with R_3SiCN . Failure to isolate pure fluoride cyanides or cyanates of tungsten is not surprising in view of the similar results obtained for the reactions of Nb and Ta pentafluorides with Me_3SiX ($\text{X} = \text{CN}, \text{NCO}, \text{SCN}$).⁶⁸

CONCLUSIONS

$\text{WF}_5\text{OC}_6\text{F}_5$ and $\text{MoF}_5\text{OC}_6\text{F}_5$ can be isolated from the reactions of WF_6 and MoF_6 with $\text{Me}_3\text{SiOC}_6\text{F}_5$ (1:1 mole ratio). The reaction of WF_6 (1 mole) with $\text{Me}_3\text{SiOC}_6\text{F}_5$ (2 moles) gives a mixture of pentafluorophenoxy tungsten(VI) fluorides, including $\text{WF}_5\text{OC}_6\text{F}_5$ and $\text{WF}_4(\text{OC}_6\text{F}_5)_2$. Unlike $\text{WF}_4(\text{OR})_2$ ($\text{R} = \text{Me}$ or Ph),⁸⁷ $\text{WF}_4(\text{OC}_6\text{F}_5)_2$ exists in both cis and trans forms. The simplest interpretation of ^{19}F n.m.r. spectra of pentafluorophenyl tungsten(VI) fluorides is that they have monomeric, octahedral structures, displaying geometrical isomerism in some cases. The difference in the ortho and para fluorine chemical shifts of pentafluorophenyl group in $\text{WF}_5\text{OC}_6\text{F}_5$ is the smallest among the reported pentafluorophenyl derivatives, which suggests that OWF_5 is an π electron acceptor group. The colour of these compounds is ascribed to intramolecular charge transfer from the pentafluorophenyl ring to non-bonding orbitals of tungsten. Further work can be directed on the nucleophilic substitution reactions of the pentafluorophenyl ring.

Carboxylato tungsten(VI) fluorides cannot be isolated from the reactions of WF_6 with $\text{Me}_3\text{SiOC}(\text{O})\text{R}$ ($\text{R} = \text{CH}_3$, CF_3 or C_3F_7), even at -80° ; the products, being unstable, decompose. The decomposition of acetates and trifluoroacetates of tungsten appears to proceed by different routes, and more work is required to confirm the mechanism for decomposition. Tungsten hexafluoride undergoes substitution reactions with Me_3SiX ($\text{X} = \text{CN}$ or NCO) but the products are not characterized.

EXPERIMENTAL

Chemicals

Molybdenum hexafluoride (Allied Chemical Co.) was purified by low temperature trap to trap distillation, over NaF. Tungsten hexafluoride (Allied Chemical Co.), and trimethylchlorosilane (B.D.H.) were purified as described previously (chapter one). The finely ground silver perfluorocarboxylates (Peninsular Chem. Research Inc.), AgCN (B.D.H.) and AgOC(O)CH_3 (B.D.H.) were dried overnight under dynamic vacuum.

$\text{Me}_3\text{SiCO}_2\text{R}$ (where $\text{R} = \text{CH}_3$, CF_3 and C_3F_7) was prepared from the reaction of Me_3SiCl on the appropriate silver carboxylate.¹³⁷ $\text{Me}_3\text{SiOC(O)R}$ was dried over activated Linde 4A molecular sieves and degassed before use. As a further check on purity their i.r. and mass spectra were compared with those reported¹³⁷ and were found identical. Me_3SiI was prepared by refluxing a mixture of $(\text{Me}_3\text{Si})_2\text{O}$ (19 mmol Koch Light Lab. Ltd.), Al fillings (5.4 gms) with I_2 (26 mmol B.D.H.).¹³⁸ The product from this reaction was distilled twice at atmospheric pressure and once over copper powder under nitrogen in diffuse light. Its boiling point was 107-108/760 mm. mercury. (Lit. value 106.8/742 mm. of mercury.)¹³⁹ It was stored in a brown flask under nitrogen. The reaction of Me_3SiCl with AgCN was reported to give 40% of Me_3SiCN .¹⁴¹ This reaction did not work in the present case; even after refluxing the mixture for a week, no Me_3SiCN could be isolated. Me_3SiCN was prepared by refluxing Me_3SiI with AgCN at 100-105°C for 10 hours.¹³⁹ The product was purified by fractional distillation. Its b.p. was 116.5-117.5°C/760 mm. Hg, which agrees with the literature value.¹³⁹ Me_3SiCN was degassed and stored over activated Linde 4A molecular sieves under vacuum. Its infra-red spectrum was identical with the reported spectrum.¹⁴⁰ Et_3SiCN was prepared by the reaction of Et_3SiBr (Phase separation) with AgCN.¹³⁹

It was dried over activated Linde 4A molecular sieves. Its i.r. spectrum showed the characteristic CEN vibration at $2195(s) \text{ cm}^{-1}$.^{85a} $\text{Me}_3\text{SiOC}_6\text{F}_5$ was prepared by Oliver's method¹⁴³ by refluxing pentafluorophenol (Ralph N. Emanuel Ltd.) with excess Me_3SiCl . It was purified by fractional distillation and dried over activated Linde 4A molecular sieves. Its ^{19}F n.m.r. spectrum was compared with the one reported¹²⁷ and was found to be identical. $(\text{CF}_3\text{CO})_2\text{O}$ (Fluorochem. Ltd.) was degassed and distilled under vacuum over activated Linde 4A molecular sieves.

Experimental procedures for handling reactants and products have been described previously (chapter one).

NOTE : The sample of Me_3SiNCO was provided by J.C. Fuggle and used as such.

REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLPENTAFLUOROPHENOXY SILANE

(a) WF_6 (24.6 mmol) was condensed on to $\text{Me}_3\text{SiOC}_6\text{F}_5$ (15.6 mmol) in a glass flask fitted with a Teflon stopcock and kept at -196° . The flask was allowed to warm slowly to 0°C when the reaction mixture changed from yellow to red. Reaction was smooth at 0° and took about half an hour to reach completion. The volatiles were removed at 20° , and were yellow. They were identified from i.r. spectroscopy as a mixture of Me_3SiF and unchanged WF_6 .^{95,96} Weight of $(\text{Me}_3\text{SiF} + \text{WF}_6)$, Found, 3.87 gm; Required for 1:1 reaction, 4.0 gm. The residue was a red liquid slightly volatile at 20° . It was pumped overnight to remove any unreacted $\text{Me}_3\text{SiOC}_6\text{F}_5$.

The red liquid was identified from its analysis as pentafluorophenoxy-tungsten(VI)pentafluoride, $\text{WF}_5\text{OC}_6\text{F}_5$. Found C, 15.8; F, 40.9; W,

40.2%; $C_6H_{10}OW$ requires, C, 15.6; F, 41.1 and W, 39.8%. Analyses for H and Si were zero.

The molecular weight of $WF_5OC_6F_5$ was determined from the lowering in vapour pressure of C_6F_6 by $C_6F_5OWF_5$. The results are given in Table 2.12.

Table 2.12

Molecular weight of $WF_5OC_6F_5$

Mole fraction of $WF_5OC_6F_5$ in C_6F_6	Molecular weight Found
0.74	518
0.56	501
0.51	496
0.50	491
0.45	479
Average = 497	
$WF_5OC_6F_5$	
Requires = 462	
(if monomeric)	

The i.r. spectrum of the liquid in the region $2000-400\text{ cm}^{-1}$ was as follows :- 1642m, 1535sh, 1530s, 1515s, 1470sh, 1365m, 1332s, 1329sh, 1260w, 1192s, 1185sh, 1165sh, 1050s, 1010sh, 1001s, 722s, 670s, 650sh, 635sh, 502w, 455w.

The Raman spectrum of the liquid contained the following absorptions

(2000-250 cm^{-1}) 1633s, 1472v.s, 1333s, 1198v.s, 1051s, 767s, 724w, 498m, 285w.

Its electronic spectrum (800-300 nm) was recorded in Me_4Si and C_6F_6 . The absorption in Me_4Si solution was observed at 345 nm. ($29.0 \times 10^3 \text{ cm}^{-1}$) and in C_6F_6 solution at 350 nm ($28.6 \times 10^3 \text{ cm}^{-1}$). The solutions were very dilute and were prepared in the inert atmosphere box. Details of the experimental procedure are given in the Appendix.

The ^{19}F n.m.r. spectrum of the neat liquid was characteristic of an AB_4 spin system. The results and assignments are given in Table (2.1).

(b) The reaction was repeated using 3.67 mmol of WF_6 and 6.8 mmol of $\text{Me}_3\text{SiOC}_6\text{F}_5$. The products were Me_3SiF , identified from i.r. spectroscopy⁹⁵ and molecular weight determinations (molecular weight, Found, 92.3; Me_3SiF requires 92.0), and a red liquid which was slightly volatile at 20° . Total weight of Me_3SiF recovered, 7.3 mmol; requires for 2:1 reaction ($\text{Me}_3\text{SiOC}_6\text{F}_5:\text{WF}_6$; 2:1), 6.8 mmol.

Elemental analysis of the liquid corresponded to bis(pentafluorophenoxy)tungsten(VI)tetrafluoride, $\text{WF}_4(\text{OC}_6\text{F}_5)_2$. Found, C, 22.8; F, 42.2; W, 29.8%; $\text{C}_{12}\text{F}_{14}\text{O}_2\text{W}$ requires C, 23.0; F, 42.5; W, 29.4%.

The ^{19}F n.m.r. spectrum of the neat liquid was consistent with the presence of more than one species. The results are summarized in Table 2.7.

The i.r. spectrum of the neat liquid in the region 2000-400 cm^{-1} contained the following absorptions : 1642m, 1530sh, 1512v.s, 1470sh, 1365m, 1335s, 1195sh, 1169s, 1035v.s, 999v.s, 920w, 785w, 724sh, 722s, 690v.s, 660v.s, 630sh, 605sh, 505w, 455w.

REACTION OF MOLYBDENUM HEXAFLUORIDE WITH TRIMETHYLPENTA-
FLUOROPHENOXYLSILANE

MoF_6 (21.03 mmol) and $\text{Me}_3\text{SiOC}_6\text{F}_5$ (5.23 mmol) were allowed to react at -60° for about 10 hours. The flask was then allowed to warm to 0° over a period of four hours and materials removed at 0° . The volatiles were colourless and consisted of a mixture of Me_3SiF and unreacted MoF_6 , identified from i.r. spectroscopy.^{95,86a} Total weight of $\text{Me}_3\text{SiF} + \text{MoF}_6$. Obtained = 4.0 gms; required for 1:1 reaction = 3.8 gms.

The residue was a metallic dark green crystalline material. It was involatile at 20° and was soluble in C_6F_6 , TMS, toluene and benzene giving orange solution. Its elemental analysis corresponded to pentafluorophenoxy molybdenum(VI) pentafluoride, $\text{MoF}_5\text{OC}_6\text{F}_5$, found, C, 19.0; F, 50.6; Mo, 25.8%; $\text{C}_6\text{F}_{10}\text{OMo}$ requires, C, 19.3; F, 50.8; Mo, 25.7%.

The electronic spectrum of $\text{MoF}_5\text{OC}_6\text{F}_5$ (800-300 $\text{m}\mu$) was recorded in Me_4Si and C_6F_6 . The absorption in Me_4Si solution observed was at 515 nm ($19.4 \times 10^3 \text{ cm}^{-1}$) and in C_6F_6 solution at 530 nm ($18.9 \times 10^3 \text{ cm}^{-1}$). Both solutions were very dilute and were prepared in an inert atmosphere box.

No n.m.r. signals could be observed for this compound in C_6F_6 solution.

The i.r. spectrum of $\text{MoF}_5\text{OC}_6\text{F}_5$ in the 2000-400 cm^{-1} region (Nujol and fluorolube mulls) was as follows : 1640m, 1515s, 1410s, 1325w, 1265w, 1225w, 1190w, 1169w, 1035m, 1001s, 977sh, 800w, 767w, 735w, 725w, 675m, 635m, 620s, 589w, 560sh, 460w.

REACTION OF TRIMETHYLSILYLACETATE WITH TUNGSTEN HEXAFLUORIDE

$\text{Me}_3\text{SiOC}(\text{O})\text{CH}_3$ (17.2 mmol) was distilled on to WF_6 (19.0 mmol) in a flask kept at -196°C . The reaction mixture was allowed to warm to 20° over a period of 10 hours, when the reactants formed a colourless solution. The solution was kept at 20° for a week but no visible signs of reaction were observed. On distilling off the volatiles however, an orange viscous liquid involatile at 20° was obtained. The volatiles were identified from infra-red spectroscopy to be unchanged WF_6 ,⁹⁶ Me_3SiF ,⁹⁵ SiF_4 ,¹⁰², CH_3COF ¹⁴⁴ and CO_2 .⁹⁷ Total weight of the volatiles obtained = 2.609 gm., requires for the 1:1 reaction of WF_6 with $\text{Me}_3\text{SiCO}_2\text{CH}_3$ = 2.119 gms.

The orange liquid dissolved in C_6F_6 giving a green solution. A reddish brown viscous material separated from the solution after 30 minutes. The ^1H n.m.r. spectrum of the green solution showed only a singlet at 2.2 p.p.m. The ^{19}F n.m.r. spectrum contained three signals, all single lines at -62.4, -47.0 and 24.9 p.p.m.

The orange liquid, kept at 20° for a week, evolved CO_2 which was identified both from i.r. spectroscopy⁹⁷ and molecular weight determinations. Molecular weight found 43.2; CO_2 requires, 44.0. Although decomposition was slow at 20° , above 40° rapid decomposition of the solid took place giving CO_2 , CH_3COF and SiF_4 , which were identified from infra-red spectroscopy.^{97,102,144} The residue from the decomposition reaction was a dark red solid which was not investigated.

Elemental analysis of the orange liquid : C, 7.3; H, 0.6; F, 29.9; W, 58.0%. Ratio of the atoms C:H:F:W = 2:2:6:1.

The infra-red spectrum of the liquid pressed between KBr plates was as follows ($4000\text{--}400\text{ cm}^{-1}$) : 3400-2940br.s, 2880br.m, 2870sh, 2305w, 2195w, 2045w, 1780br,w, 1670w, 1615w, 1440br,m, 1220br,m, 1170w, 1030sh,

1020s, 990sh, 932w, 895w, 850w, 700w, 620br.m, 550br.w, 450br.m.

(b) WF_6 (21.2 mmol) and $\text{Me}_3\text{SiOC}(\text{O})\text{CH}_3$ (20.9 mmol) were kept at -80° for 24 hours. The fraction volatile at -80° was identified as a mixture of Me_3SiF and CH_3COF by i.r. spectroscopy.^{95,144} The flask was warmed to 0° and the volatiles which separated at this temperature were identified as Me_3SiF , MeCOF , CO_2 and unchanged WF_6 by i.r. spectroscopy.^{95,96,97,144} Total weight of the volatiles obtained = 3.06 gms; requires for 1:1 reaction = 2.07 gms.

The residue was an orange oily liquid. It dissolved in C_6F_6 giving a green solution and finally a reddish brown mass. The ^1H n.m.r. spectrum of the solution consisted of a complex set of signals at 2.2 p.p.m. and a very weak broad signal at 6.4 p.p.m. Its ^{19}F n.m.r. spectrum contained three signals, all single lines at -62.4, -47.0 and 24.9 p.p.m.

Elemental analysis of the liquid was as follows : C, 6.4; H, 0.7; F, 25.8; W, 50.6; O (by difference), 16.5%. Ratio of the atoms $\text{C:H:F:W:O} = 2:3:5:1:3$.

The infra-red spectrum of the neat liquid in the region $4000\text{--}400\text{ cm}^{-1}$ contained the following absorptions : 3350br.s, 3160w, 3040w, 2990w, 2550w,br, 2355s, 2250s, 1790w, 1670sh, 1665s, 1620s, 1550s, 1510sh, 1405w, 1320sh, 1330w, 1285w, 1135br.m, 1185w, 1040sh, 1025s, 990w, 920w, 855w, 650s, 605sh, 550m, 465m.

The above reaction was repeated three times and similar results were obtained.

REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLSILYLTRI-
FLUOROACETATE

A mixture of WF_6 (12.1 mmol) and $\text{Me}_3\text{SiOC(O)CF}_3$ (7.44 mmol) gave a colourless solution at 0° and no change in the solution was observed, even after 15 days at 20° . A mixture of light brown solid and white needle like crystals was obtained after distilling off unreacted WF_6 and other volatiles at 20° . Me_3SiF , $^{95}\text{SiF}_4$ and $(\text{CF}_3\text{CO})_2\text{O}$ were identified from infra-red and ^{19}F n.m.r. spectroscopy. (The ^{19}F n.m.r. chemical shift for $(\text{CF}_3\text{CO})_2\text{O}$ found was 75 p.p.m.).

The solid gave a green solution in C_6F_6 , but the crystalline portion was apparently insoluble. No ^1H n.m.r. signal was observed for the solution and its ^{19}F n.m.r. spectrum consisted of five singlets at -71.3, -49.5, -14.3, 20.5 and 74.5 p.p.m.

Elemental analysis of the solid mass corresponded to oxotetrafluoro-tungsten(VI), WOF_4 . Found, F, 27.8 and W, 66.5%; WOF_4 requires, F, 27.6, W, 66.7%.

The i.r. spectrum of the solid in 2000-400 cm^{-1} region (Nujol and fluorolube mulls) was as follows : 1748m, 1680s, 1462sh, 1458s, 1443, 1430sh, 1380w, 1267s, 1245w, 1195s, 1048s, 860s, 790w, 767m, 728sh, 718m, 660s, br, 630s, br, 620sh, 569m, 540sh, 438w.

REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLSILYLPERFLUORO-
BUTYRATE

WF_6 (8.7 mmol) was reacted with $\text{Me}_3\text{SiOC(O)C}_3\text{F}_7$ (5.0 mmol) at -80° for a week. On distilling off the volatiles at 20° a trace amount of orange powder was left on the walls of the reaction vessel. The volatiles

were Me_3SiF and SiF_4 identified from their i.r. spectra,^{95,102}

Unreacted WF_6 and $\text{Me}_3\text{SiOC(O)C}_3\text{F}_7$ were recovered from this reaction.

The powder was partially soluble in C_6F_6 giving a green solution. The ^{19}F n.m.r. spectrum of this solution contained two singlets at -46.6 and +26.0 p.p.m.; 3 sets of complex peaks at 116.8, 120.1 and 124.3 p.p.m. and a complex weak signal at 80.00 p.p.m.

Since the amounts recovered were insufficient, further investigations of the powder by i.r. spectroscopy or elemental analysis were impossible.

REACTION OF METHOXYTUNGSTEN(VI)PENTAFLUORIDE WITH TRIFLUORO- ACETIC/ANHYDRIDE

WF_5OMe (6.1 mmol) dissolved in $(\text{CF}_3\text{CO})_2\text{O}$ (7.8 mmol) giving a pale yellow solution. The ^1H n.m.r. of this solution consisted of a singlet at 3.91 p.p.m. Its ^{19}F n.m.r. spectrum contained the signals at -65.6(s), -14.8br, 74.7(s) and 145.6(s) p.p.m. The reaction mixture darkened to brown on heating. There was no change in the ^1H n.m.r. of this solution but ^{19}F n.m.r. spectrum contained two additional signals, both single lines, at -114.1 and 133.0 p.p.m. A low melting brown solid and white crystals were left after distilling volatiles off from the reaction flask. The volatiles were identified as CF_3COF and unreacted $(\text{CF}_3\text{CO})_2\text{O}$ from their i.r. spectra.^{145,146}

The residue was partially soluble in C_6F_6 giving a green solution. The ^1H n.m.r. spectrum of this solution consisted of two singlets at 3.67 and 5.28 p.p.m. Its ^{19}F n.m.r. spectrum had three signals, all single lines at -68.4, -48.4 and 17.0 p.p.m.

REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIALKYLSILYL CYANIDES

(a) WF_6 (13.3 mmol) and Me_3SiCN (5.7 mmol) reacted within 30 minutes at 20° to give a black fluffy powder. The volatiles separated at 20° were Me_3SiF , SiF_4 and unreacted WF_6 identified from i.r. spectroscopy.^{95,96,102}

The residue was insoluble in C_6F_6 , toluene, CS_2 , CCl_4 , CHCl_3 , CH_3CN , CH_3NO_2 , acetone and hexane. Its elemental analysis was consistent with the presence of some Me_3SiCN . Found, C, 14.2; H, 1.6, N, 12.4, F, 11.5, W, 55.1 and Si, 1.3%.

Oxidation titrations with KMnO_4 solution gave irreproducible results, but indicated that the oxidation number of W was less than six. The magnetic moment of residue, was found to be 0.0 B.M.

Its i.r. spectrum (Nujol and fluorolube mulls) in the $400\text{--}400\text{ cm}^{-1}$ region was as follows : 2970w, 2940w, 2150m, 1650br,w, 1300w, 1258w, 1210w, 1160w, 995w, 970w, 890w, 850w, 730m, 600br,w.

(b) The products of the reactions between Et_3SiCN (7.8 mmol) and WF_6 (12.3 mmol), and Me_3SiCN and WF_6 were similar. The volatiles from the former reactions were found to be Et_3SiF ,¹⁴⁷ unreacted WF_6 ⁹⁶ and an unidentified compound containing a CN group (not Et_3SiCN) characterized by a band of medium intensity at about 2280 cm^{-1} in the i.r. spectrum. The total weight of the volatiles obtained was 4.02 gms.

Elemental analysis of the black powder (two samples from separate experiments) was as follows : Found, C, 15.3 and 15.7; H, 1.1 and 1.6; N, 13.2 and 10.9; F, 11.8 and 9.9; W, 57.4 and 48.9%.

The products of reactions (a) and (b) behaved similarly towards solvents and oxidising agents, and gave similar infra-red spectra.

The hydrolysis of the powder was investigated by dissolving it in degassed, distilled water. At 20° volatiles were distilled from the brown solution and were found to be H₂O,⁹⁷ HCN⁹⁷ and an unidentified compound containing the carbonyl group, characterized by a broad band at 1847 cm⁻¹ in the infra-red spectrum. The following possibilities for the unidentified product were excluded on the basis of the comparison of the i.r. spectra with reported spectra.

HCCF, HCO₂H;¹⁴⁸ (FCO)₂, F₂CO;¹⁴⁹ FCO;¹⁵⁰ FCN, HNCO;¹⁵¹
R₃SiOH¹⁵² and (R₃Si)₂O.¹⁵³

The mass spectrum of the volatiles contained the following main peaks corresponding to m/e : 11-16, 26-29, 45, 47, 48, 52, 72, 73, 77, 83-92, 97, 105, 117, 134 and 145.

No n.m.r. signals could be obtained for these volatiles.

The black powder gave (CN)₂, (identified by i.r. spectroscopy)⁹⁷ on heating above 80° but the nature of residue was not investigated.

REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLSILYLISOCYANATE

WF₆ (18.4 mmol) and Me₃SiNCO (18.5 mmol) reacted smoothly at 20° giving an orange solid. The reaction was complete within half an hour. The volatiles identified from i.r. spectroscopy were Me₃SiF,⁹⁵ SiF₄¹⁰² and unreacted WF₆.⁹⁶ The total weight of the volatiles obtained was 1.95 gms.

The residue was insoluble in CH₃NO₂, CH₃CN, (CH₃)₂CO, CHCl₃, CCl₄, C₆F₆, CS₂, CCl₃F, Me₄Si toluene and hexane.

Elemental analysis (two samples from separate experiments). Found C, 9.3 and 7.9; H, 0.0 and 0.8; N, 6.9 and 8.8; F, 0.0 and 6.5; W, 46.3 and 46.0; O (by difference), 37.5 and 30.0%.

Ratio of the atoms : C:H:N:P:W:O = 3.1, 2.7:-, 3.1:2.0, 2.5: ~
1.4:1, 1:2.3, 7.5

Its infra-red spectrum in the 4000-400 region (Nujol and fluorolube mulls) was as follows : 2970m, 2950w, 2220sh, 2180br, 1650br,w, 1260br,w, 1140br,w, 1070br,w, 1010w,br, 890v,w, 850v.w, 790sh, 770sh, 722m, 650sh, 605m.

It gave $(\text{CN})_2^{97}$ on heating above 80°C. The residue from the thermal decomposition reaction was a red solid, which was not investigated

CHAPTER THREE

FLUORINE-18 EXCHANGE BETWEEN TRIMETHYLFUOROSILANE AND SUBSTITUTED DERIVATIVES OF TUNGSTEN HEXAFLUORIDE

INTRODUCTION

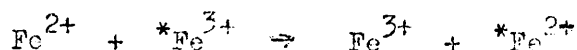
Naturally occurring radioactive isotopes such as ^{210}Pb and ^{232}Th were used before 1934 to investigate the movement of atoms during suitable chemical reaction.¹¹² Since then radionuclides of the more familiar and useful lighter elements have been obtained from nuclear reactions. This has led to many experiments in which radioisotopes have been used to obtain information on reaction mechanisms.¹⁴²

Much of the early work was designed to obtain information regarding the nature and strength of bonds. It was assumed that an ionic bond would interchange groups or atoms more readily than a covalent bond and that, for a series of bonds of similar type, the weakest bond would interchange most readily. Many reactions, for example, the reactions of Co(II) with substituted salicylaldehyde and phthalocyanine, were interpreted on such a basis.¹⁵⁴

The mechanisms of isotopic exchange reactions are closely related to those of substitution reactions. In the former, atoms of a given element interchange between two or more species, without the formation of new species or alteration in concentration. A typical reaction is described by the equation :



and may occur either by exchange of an atom or a group, or by exchange of electrons,^{112,142} for example



Isotopic labelling (indicated by an asterisk in the equations) provides one of the few techniques for distinguishing atoms of the same element. It is a convenient method of studying such reactions.

In this work, a technique has been developed for investigating the exchange of fluoride ligands between trimethylfluorosilane and substituted tungsten(VI) fluorides using ^{18}F radioactive tracers. Despite the large amount of work on fluorine and its compounds since 1940, little use has been made of fluorine isotopes for studying chemical reactions and physical changes.¹⁵⁵ Fluorine occurs in nature only in the form of the stable nuclide ^{19}F . The radioactive isotopes ^{17}F , ^{18}F and ^{20}F have been prepared but ^{18}F is the only isotope of fluorine which is sufficiently long-lived (half-life 112 mins.) to serve as a tracer.¹⁵⁶ This nuclide was first described by Snell¹⁵⁷ in 1937, as a product of the bombardment of neon gas with 5-MeV deuterons and by Pool, Cork and Thornton¹⁵⁸ from the reaction $^{19}\text{F}(\text{n}, 2\text{n})^{18}\text{F}$. Since that time, it has been shown that ^{18}F can be produced by a wide variety of nuclear reactions.^{155,156,159} Only a few of these methods, however, yield a product of high radiochemical purity and relatively high specific activity. The choice of preparative method and target material depends upon the high-energy machine available and the subsequent treatment of the sample for extraction of the ^{18}F . The most useful method of obtaining carrier free - ^{18}F is from the sequence of reactions, $^{156}\text{}^6\text{Li}(\text{n}, \alpha)\text{t}$; $^{16}\text{O}(\text{t}, \text{n})^{18}\text{F}$.

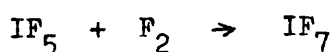
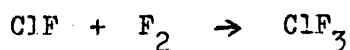
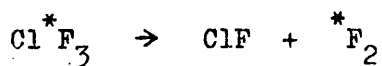
The nuclide ^{18}F emits an 0.65 MeV positron which is usually detected by means of the associated pair of annihilation gamma rays. Any method normally used for detecting γ -rays may then be employed. ^{18}F has been counted in the form of a solid as PbClF , or NaF , a liquid as HF , and in

various gases such as HF, F₂, ClF₃, BrF₅ and IF₇.¹⁶⁰

One of the earliest uses of ¹⁸F in chemical exchange studies was by Dodgen and Libby¹⁶¹ who employed this isotope in the study of the gas-phase exchange between fluorine and hydrogen fluoride. This preliminary study indicated that at 200°C there was a measureable amount of exchange, probably taking place on the walls of the brass container.

Rogers and Katz¹⁶¹ examined both the liquid phase and gas-phase exchange reactions of HF with SbF₅ and the halogen fluorides, ClF₃, BrF₃, BrF₅, IF₅. The exchange was rapid in both the gas-phase and the liquid-phase at room temperature. It was postulated that the reaction took place via a homogeneous mechanism involving the formation of intermediate donor acceptor complexes.

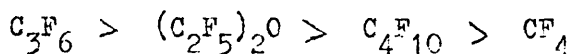
Quantitative kinetic studies of the gas-phase exchange between F₂ and the halogen fluorides ClF₃, BrF₅, IF₇,¹⁶² and between F₂ and HF have been carried out in the temperature range of 200-300°C.¹⁶³ It was postulated that for the ClF₃-F₂ and IF₇-F₂ reactions the exchange occurred by a combined heterogeneous mechanism of the competitive type, and a homogeneous mechanism involving the dissociation of the halogen fluoride.



In the case of the BrF₅-F₂ reaction, the exchange was suggested to take place by heterogeneous catalysis involving the metal fluoride coating on the walls of the reaction vessel.¹⁶²

Gens¹⁶⁴ studied the isotopic exchange between solid inorganic fluorides

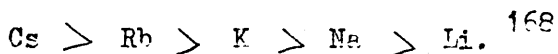
and some gaseous fluorocarbons. Among the inorganic fluorides, exchange was found to be most rapid with the alkali metal fluorides and increased with increasing atomic number of the alkali metal. The rate of exchange of the gaseous fluorocarbons followed the order :



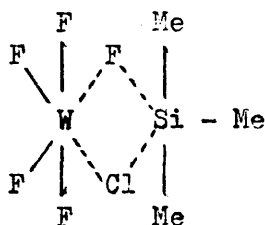
Sheft and Hyman¹⁶⁵ examined the exchange reactions of the hexafluorides of sulphur, xenon, molybdenum, tungsten, osmium, iridium and uranium with fluorine in the gas phase. The least reactive fluoride was sulphur hexafluoride which did not exchange at temperatures up to 350°. (The exchange between isotopically labelled HF and SF₆ at 27°, however, has been found to be 10% after 3 minutes, in the gaseous phase).¹⁶¹ The most reactive was xenon hexafluoride for which the rates of exchange at 100° and 150° have been measured. The rate of exchange was found to be a linear function of the fluorine concentration, so that the reaction, if homogeneous, appeared to have an associative mechanism.¹⁶⁶ Osmium hexafluoride exchanged under similar conditions and the reaction was strongly dependent on the fluorine concentration : the results for iridium hexafluoride did not show this dependence and the dissociative mechanism had an activation energy of about 12 Kcal.mol.⁻¹ Tungsten hexafluoride and molybdenum hexafluoride have been reported to exchange rapidly with fluorine in the gas-phase, but the results have not been published in full.¹⁶⁶ No exchange was observed between gaseous UF₆ and Li¹⁸F, K¹⁸F, Zr¹⁸F₄ and Ag¹⁸F up to 350°C. Significant exchange was noted, however, between UF₆ and Na¹⁸F and Ca¹⁸F₂ at 350°C. The results in the former case were explained in terms of a compound Na₂UF₈, but no such compound was formed in the latter case.¹⁶⁵

¹⁸F labelled BF₃, SiF₄, PF₅, POF₃, AsF₅, SF₄, SOF₂ and SeF₄ have been prepared by passing the gases over heated Li¹⁸F at about 200°C. In these

reactions the exchange was suggested to occur via the formation of an unstable intermediate between LiF and the covalent fluoride.¹⁶⁷ Very recently the exchange between group I fluorides (Cs-Li inclusive) and trifluoroacetyl fluoride or SF₄ at 150° and 50° has been observed. The order of exchange in these reactions has been found to be



As described in the previous two chapters the organosilanes, R₃SiX (R = Me, Et; X = Cl, OMe, OPh, OC₆F₅ and NR₂) have been extensively used for the preparation of substituted derivatives of covalent halides. These reactions have been proposed by some workers, to proceed through an intermediate Lewis acid, Lewis base complex. Thus the reaction of WF₆ with Me₃SiCl is believed to involve the formation of a seven co-ordinate intermediate,



which dissociates to WF₅Cl + Me₃SiF. (Further reaction of WF₅Cl with Me₃SiCl or the re-arrangement of the chlorofluorides of tungsten gives other members of the series WF_{6-n}Cl_n, n = 0-6).⁵⁰ The formation of such complexes of WF₆ is not surprising since seven co-ordinate complexes of tungsten are known.⁴¹ However, there have been no attempts to verify these postulated mechanisms experimentally. The present work involving the study of the exchange reactions between Me₃Si¹⁸F and substituted derivatives of tungsten hexafluoride was undertaken with the intention of developing a technique to obtain quantitative kinetic data which would lead to the elucidation of the mechanisms of the reactions of tungsten

hexafluoride with the organosilanes. To test the applicability of the technique, systems in which both the substituent and the degree of substitution were varied have been investigated.

RESULTS

¹⁸F EXCHANGE OBSERVED BETWEEN SUBSTITUTED TUNGSTEN COMPOUNDS AND LABELLED TRIMETHYLELPHOSILANE AT ROOM TEMPERATURE.

The results of exchange reactions between $\text{Me}_3\text{Si}^*\text{F}$ and inactive substituted derivatives of tungsten hexafluoride are given in Tables 3.1-3.7. Active samples of $\text{Me}_3\text{Si}^*\text{F}$ are obtained by maintaining a mixture of active Cs^*F (solid) and inactive $\text{Me}_3\text{Si}^*\text{F}$ (liquid) at 50° for thirty minutes. All the exchange reactions between $\text{Me}_3\text{Si}^*\text{F}$ and the substituted tungsten compounds were carried out at room temperature, $22 \pm 3^\circ\text{C}$, except where mentioned. Two types of systems are described. These are the heterogeneous systems in which $\text{Me}_3\text{Si}^*\text{F}$ is in contact with the tungsten compound and the homogeneous systems in which $\text{Me}_3\text{Si}^*\text{F}$ is added to a solution of the tungsten compound in C_6F_6 . No exchange is observed, up to 50°C between the inactive solvent C_6F_6 and $\text{Me}_3\text{Si}^*\text{F}$, Cs^*F or labelled WF_5OMe .

In general, in the homogeneous systems the substituted tungsten compounds readily undergo ¹⁸F exchange. The exchange is easily measurable and, for each system, gives reproducible exchange rates. Two exceptions are found in the present work. $\text{WF}_2(\text{OMe})_4$ is the least reactive among the tungsten compounds studied. Even after 180 minutes no exchange is observed at $22 \pm 3^\circ\text{C}$. The exchange reaction of WF_5NMe_2 cannot be performed under homogeneous conditions since it is insoluble in all suitable solvents.

The fraction of ¹⁸F exchanged (\underline{f}) is calculated from the expression:¹⁶²

$$\underline{f} = \frac{A_1}{A_1 + A_2} \bigg/ \frac{n_1 m_1}{n_1 m_1 + n_2 m_2} \quad (3.1)$$

Table 3.1

^{18}F Exchange between labelled Me_3SiF and WF_5NET_2 at room temperature (heterogeneous system)

S.No	WF_5NET_2 (mmol)	Me_3SiF (mmol)	Activity of Me_3SiF at t_0 CPS	Activity of Me_3SiF after exchange CPS	Activity of WF_5NET_2 after exchange CPS	Total activity after exchange CPS	Time (mins.)	Fraction Exchange \bar{f}
1	0.82	1.1	4,737	1,690	1,820	3,510	30	0.658 ± 0.002
2	1.33	1.66	8,126	2,370	2,373	4,743	70	0.625 ± 0.002
3	0.64	0.63	760	137	320	457	75	0.838 ± 0.002
4	4.57	5.2	22,270	8,353	2,883	11,083	120	0.319 ± 0.001
5	1.42	1.31	1,340	124	270	394	210	0.812 ± 0.006

Table 3.2.

¹⁸F Exchange between labelled Me₃SiF and WF₅OMe at room temperature (heterogeneous system)

S.No	WF ₅ OMe (mmol)	Me ₃ SiF (mmol)	Activity of Me ₃ SiF at t ₀	Activity of Me ₃ SiF after exchange	WF ₅ OMe after exchange	Total activity after exchange	Time (mins)	Fraction Exchange
			CPS	CPS	CPS	CPS		f
1	2.0	4.4	13,437	7,293	4,562	11,855	15	0.554 ± 0.002
2	7.0	9.7	48,200	36,917	1,780	38,697	30	0.059 ± 0.0002
3	1.5	2.4	9,207	1,820	4,014	5,844	60	0.907 ± 0.002
4	4.8	4.8	24,400	11,616	5,820	17,436	60	0.401 ± 0.005
5	3.7	3.7	91,400	15,936	26,055	41,991	120	0.745 ± 0.004

F Exchange between labelled Me_3SiF and WF_5OME in C_6F_6 solution at room temperature.

S.No	Molality of Activity of				Activity of		Total activity	Time (mins)	Fraction Exchange $\frac{f}{1-f}$	Log $\left(\frac{1}{1-f}\right)$
	WF_5OME	Me_3SiF	Me_3SiF at t_0	CPS	Me_3SiF	WF_5OME				
after exchange after exchange										
			CPS	CPS	CPS	CPS				
1	1.361	1.977	853	587	103	690	30	0.193 ± 0.002	0.093	
2	1.276	1.233	3,755	890	869	1,759	80	0.589 ± 0.002	0.386	
3	1.363	1.563	6,988	1,280	1,645	2,925	120	0.691 ± 0.002	0.511	
4	1.435	1.473	5,346	617	1,358	1,975	155	0.829 ± 0.003	0.767	
5	1.373	1.515	1,327	110	265	375	190	0.863 ± 0.007	0.863	
6	1.583	1.374	8,645	522	1,588	2,110	210	0.883 ± 0.003	0.933	

Table 3.4

^{18}F Exchange between labelled Me_3SiF and $\text{WF}_5\text{OC}_6\text{F}_5$ in C_6F_6 solution at room temperature.

S.No	Molality of Activity of				Activity of		Total	Time Fraction		$\text{Log}\left(\frac{1}{1-f}\right)$
	$\text{WF}_5\text{OC}_6\text{F}_5$	Me_3SiF	Me_3SiF at t_0	after exchange	Me_3SiF	$\text{WF}_5\text{OC}_6\text{F}_5$		(mins)	Exchange	
			CPS		CPS	CPS				
1	0.223	0.180	110	68	10	78	30	0.160 \pm 0.005	0.076	
2	0.399	0.319	494	301	80	381	30	0.244 \pm 0.003	0.121	
3	0.415	0.459	1,862	1,163	239	1,402	30	0.208 \pm 0.001	0.101	
4	0.401	0.578	1,977	1,040	190	1,230	60	0.199 \pm 0.002	0.096	
5	0.553	0.677	3,653	1,318	231	1,549	120	0.186 \pm 0.001	0.089	

¹⁸F Exchange between labelled Me₃SiF and WF₅Oph in C₆F₆ solution at room temperature.

S.No	Molality of Activity of				Total activity	Time (mins)	Fraction Exchange	Log (1/(1-f))
	WF ₅ Oph	Me ₃ SiF	Me ₃ SiF at t ₀	after exchange after exchange				
			CPS	CPS			f	
1	0.686	0.763	1,945	1,223	1,488	30	0.218 ± 0.001	0.11
2	0.725	0.720	4,063	2,058	2,638	60	0.264 ± 0.001	0.13
3	0.723	0.731	5,345	1,319	2,040	140	0.425 ± 0.002	0.24
4	1.34	1.354	236	155	187	30	0.206 ± 0.004	0.10
5	1.413	1.458	256	116	147	80	0.254 ± 0.005	0.13
6	1.356	1.417	302	73	105	160	0.369 ± 0.007	0.20

Table 3.6

^{18}F Exchange between labelled Me_3SiF and $\text{cis-WF}_4(\text{OMe})_2$ in C_6F_6 solution at room temperature

S.No	Molality of Activity of			Activity of		Total Activity	Time (mins)	Fraction
	$\text{cis-WF}_4(\text{OMe})_2$	Me_3SiF	Me_3SiF at t_0	Me_3SiF after exchange	$\text{cis-WF}_4(\text{OMe})_2$ after exchange			
			CPS	CPS	CPS			$\text{Exchange Log} \left(\frac{1}{1-f} \right)$
1	1.053	1.149	4,543	2,190	1,195	3,385	30	0.449 ± 0.002
2	0.702	0.650	2,890	580	1,060	1,640	60	0.796 ± 0.003
3	2.319	2.693	7,696	924	2,890	3,814	95	0.981 ± 0.002
4	0.865	0.809	4,030	480	1,100	1,580	125	0.860 ± 0.003
5	2.067	2.087	7,053	520	1,904	2,424	160	0.984 ± 0.003

Table 3.7

^{18}F Exchange between labelled Me_3SiF and $\text{WF}_2(\text{Net}_2)_4$ in C_6F_6 solution at room temperature.

S.No	Molality of Activity of				Activity of		Total	Time	Exchange	$\text{Log}\left(\frac{1}{1-f}\right)$
	$\text{WF}_2(\text{Net}_2)_4$	Me_3SiF	Me_3SiF at t_0	after exchange	Me_3SiF	$\text{WF}_2(\text{Net}_2)_4$				
		CPS			CPS	CPS		(mins)	f	
1	0.219	935	587	16	603	60	0.042 \pm	0.019	0.001	
2	0.282	2,088	447	77	524	180	0.224 \pm	0.111	0.003	
3	0.241	2,247	378	84	462	240	0.269 \pm	0.137	0.003	
4	0.750	2,239	637	152	789	150	0.286 \pm	0.146	0.003	
5	0.775	5,957	1,027	312	1,339	210	0.408 \pm	0.228	0.003	
6	0.614	1,750	140	175	351	240	0.866 \pm	0.872	0.008	
7	0.442	930	265	86	315	120	0.377 \pm	0.205	0.005	
8	0.379	2,330	873	73	954	120	0.133 \pm	0.061	0.002	

Note : All the fluoride ligands of tungsten compounds are assumed to be exchangeable. This

is further discussed in the text.

CPS, counts per second; No exchange was observed between labelled tungsten compounds and C_6F_6 or active CsF and C_6F_6 .

Where A = activity (CPS) corrected for decay after exchange;

$n(\text{mol})$ = quantity of a species with n exchangeable fluoride ligands (the value of n for Me_3SiF is 1); and subscripts 1 and 2 refer to the initially inactive and active species respectively. In this case 1 refers to the tungsten compound and 2 refers to $\text{Me}_3\text{Si}^*\text{F}$. Errors in f due to weighings are estimated to be negligible and those quoted arise from count rate determinations. The equation used for the determination of these errors is :¹⁷¹

$$\sigma = \sqrt{\frac{1}{A_1 t} + \frac{1}{(A_1 + A_2) t'}} \quad (3.2)$$

where σ is the standard deviation, A_1 and A_2 are the total number of counts for the Me_3SiF and tungsten compound respectively, and t and t' are the counting times for the two compounds.

The calculations of the fraction exchange, f are based on the assumption that all fluoride ligands of the tungsten compounds are exchangeable. However, the validity of this assumption is questionable in some cases. The substituted tungsten fluorides contain two non-equivalent types of fluoride ligands, those trans to a fluoride and those trans to a substituent. Thus, there are three possibilities, firstly, that all the fluoride ligands are exchangeable, although the two types could exchange at different rates, secondly, that only fluorides trans to a fluoride ligand are exchangeable and, thirdly, that only fluorides trans to substituents are exchangeable.

Assuming the exchange is complete after the longest time of contact in each case, it is possible to determine the number of exchangeable fluoride ligands from the fraction exchange calculated on the basis of all the three possibilities. For example, for WF_5X ($\text{X} = \text{NMe}_2, \text{OMe}, \text{CPh}, \text{OC}_6\text{F}_5$) the three possibilities are as follows : all five ligands are exchangeable, the four fluoride ligands trans to fluoride are exchangeable or the one fluoride ligand trans to X is exchangeable. Theoretically the fraction

exchange, f , is one. The experimental results, for the last possibility ($n = 1$), however, lead to the calculated f values of 1.4 and 1.8 for WF_5NET_2 and WF_5OMe respectively so this possibility is excluded. The fraction exchange calculated from experimental results on the basis of four or five exchangeable fluoride ligands is 0.92 and 0.88 respectively for WF_5OMe and 0.84 and 0.81 respectively for WF_5NET_2 . The exchange may not be complete even after the longest time of contact. Further, the difference in the two values of f for WF_5OMe and WF_5NET_2 is small. Hence it is not reasonable to decide unambiguously between the possibilities of 4 or 5 exchangeable fluoride ligands for these two compounds. For $WF_4(OMe)_2$ and $WF_2(NEt_2)_4$ there are only two possibilities, either all the fluoride ligands are exchangeable or two fluoride ligands of $WF_4(OMe)_2$ and one of $WF_2(NEt_2)_4$ are exchangeable. The latter leads to f values calculated from the experimental results of 1.18 and 1.2 respectively. Experimentally, fraction exchange calculated on the basis of the former are 0.93 and 0.87 respectively. Thus for these two compounds it seems more likely that all the fluoride ligands undergo exchange.

The exchange between Me_3Si^*F and WF_5OPh or $WF_5OC_6F_5$ is small but easily measurable. The exchange for $WF_5OC_6F_5$ appears to be almost constant and rapid. The values of f calculated from experimental results, on the assumption that one or five fluoride ligands of this compound are exchangeable, range from 0.29-0.38 and 0.16-0.24 respectively. It is obvious that exchange is not complete even for one fluoride ligand, hence it is not reasonable to decide the number of exchangeable fluorides for $WF_5OC_6F_5$. Similar conclusion apply to WF_5OPh where the exchange is slow.

Exchange Under Heterogeneous Conditions

No regular trends in the exchange reactions of the heterogeneous systems of WF_5NET_2 and WF_5OMe with Me_3Si^*F are discernible. The extent

of exchange appears to depend significantly on the total concentration of the reactants, the exchange being least for larger amounts of the reactants. Thus, the exchange when the total amounts of the reactants ($\text{WF}_5\text{NET}_2 + \text{Me}_3\text{Si}^*\text{F}$) is 1.27 mmol is approximately 84% ($f = 1$ is taken as 100% exchange) after 75 minutes, contrasted with approximately 32% exchange for 9.77 mmol of ($\text{WF}_5\text{NET}_2 + \text{Me}_3\text{Si}^*\text{F}$) after 120 minutes. Similarly, exchange for 3.9 mmol of ($\text{WF}_5\text{OMe} + \text{Me}_3\text{SiF}$) is approximately 91%, while it is approximately 40% for 9.6 mmol of ($\text{WF}_5\text{OMe} + \text{Me}_3\text{Si}^*\text{F}$), both after 60 minutes. Exchange also depends on the stoichiometry of the reactants. For example, the exchange observed for $\text{WF}_5\text{OMe}-\text{Me}_3\text{Si}^*\text{F}$ at a mole ratio of 1:2 is 55% after 15 minutes, contrasted with approximately 40% exchange for 1:1 stoichiometry after 60 minutes. This dependence of the rate of exchange on the concentration of reactants is not surprising in view of the fact that the exchange in a heterogeneous system largely depends on the available surface area of the compound.¹⁴² The dimensions of the reaction ampoule restrict the surface area of solid tungsten compound in contact with $\text{Me}_3\text{Si}^*\text{F}$ when large amounts of reagents are used.

Exchange Reactions under Homogeneous Conditions

One of the common features of exchange reactions in homogeneous media appears to be the dependence of the rate of reaction on the concentration of tungsten compounds. For concentrated solutions the exchange is greater than for dilute solutions. For example for a 0.76 ± 0.1 molal solution of $\text{WF}_2(\text{NET}_2)_4$ the exchange observed after 150

FOOT-NOTE : The results of exchange reactions used throughout this chapter, for comparative purposes, are those given in Tables (3.1 - 3.7), except where mentioned.

and 240 minutes is 41 and 87% respectively. In contrast, the exchange observed for an 0.24 molal solution of $WF_2(NEt_2)_4$ after 240 minutes is only 29%. Similarly, for $WF_4(OMe)_2$ the exchange observed for a 2.32 molal solution after 95 minutes is 98% compared with 86% exchange for a 0.87 molal solution after 125 minutes.

Qualitative Comparisons of the Rates of Exchange of Fluoride Ligands in Substituted Tungsten(VI) Fluorides

Since the work described in this chapter is of a preliminary nature, comparable concentrations are not available. Hence, a quantitative comparison of the rates of exchange of fluoride ligands in substituted tungsten(VI) fluorides studied is impossible. A qualitative comparison, however, suggests that $WF_4(OMe)_2$, WF_5OMe and WF_5NEt_2 are most reactive, the exchange being fast and almost complete in these compounds. In contrast of WF_5OPh and $WF_5OC_6F_5$ the exchange is very small and slow. The exchange of fluoride ligands in $WF_2(NEt_2)_4$ is intermediate. This comparison of the exchange rates suggests that ^{18}F exchange between substituted tungsten(VI) fluorides and Me_3Si^*F depends on the number and nature of substituents other than fluoride.

DISCUSSION

The rate of exchange of fluorine, at a particular temperature, in the reaction :



(where the asterisk indicates labelled F; $\text{X} = \text{NEt}_2, \text{OMe}, \text{OPh}, \text{OC}_6\text{F}_5$ and $n = 1-4$) may be expressed in terms of the concentration of reactants in dynamic equilibrium at time t , by a modified form of McKay's equation :¹⁷²

$$R = \frac{2.303}{t} \left(\frac{na}{na + nb} \right) \text{Log} \left(\frac{1}{1-f} \right) \quad (3.3)$$

where R is the rate of exchange in moles $\text{Kgms}^{-1} \text{min}^{-1}$; t is the time of exchange in minutes, a is the molality of the tungsten compound with n equivalent exchangeable fluorines, b is the molality of Me_3SiF and f is the fraction exchange, as defined by expression (3.1).

Plots have been made of $\log \left(\frac{1}{1-f} \right) \underline{y}t$ (Figs. 3.1.-3.3) for the exchange reactions in solutions of tungsten compounds and $\text{Me}_3\text{Si}^*\text{F}$. Approximately 1:1 ratios of $\text{WF}_{6-n}\text{X}_n:\text{Me}_3\text{SiF}$ were used. Results used for these plots are taken from those sets of experiments where comparable concentrations are available. The plots of $\log \left(\frac{1}{1-f} \right) \underline{y}t$ are only completely reliable in the case of WF_5OMe , where the data are obtained from four separate experiments. Three points only are available for the other plots in Fig. 3.1-3.3, although, in most cases, they are obtained from different experiments. More work is therefore needed to establish these curves unambiguously.

If all the exchangeable fluoride ligands in a tungsten compound exchange at the same rate, the plots of $\log \left(\frac{1}{1-f} \right) \underline{y}t$ is expected to be a

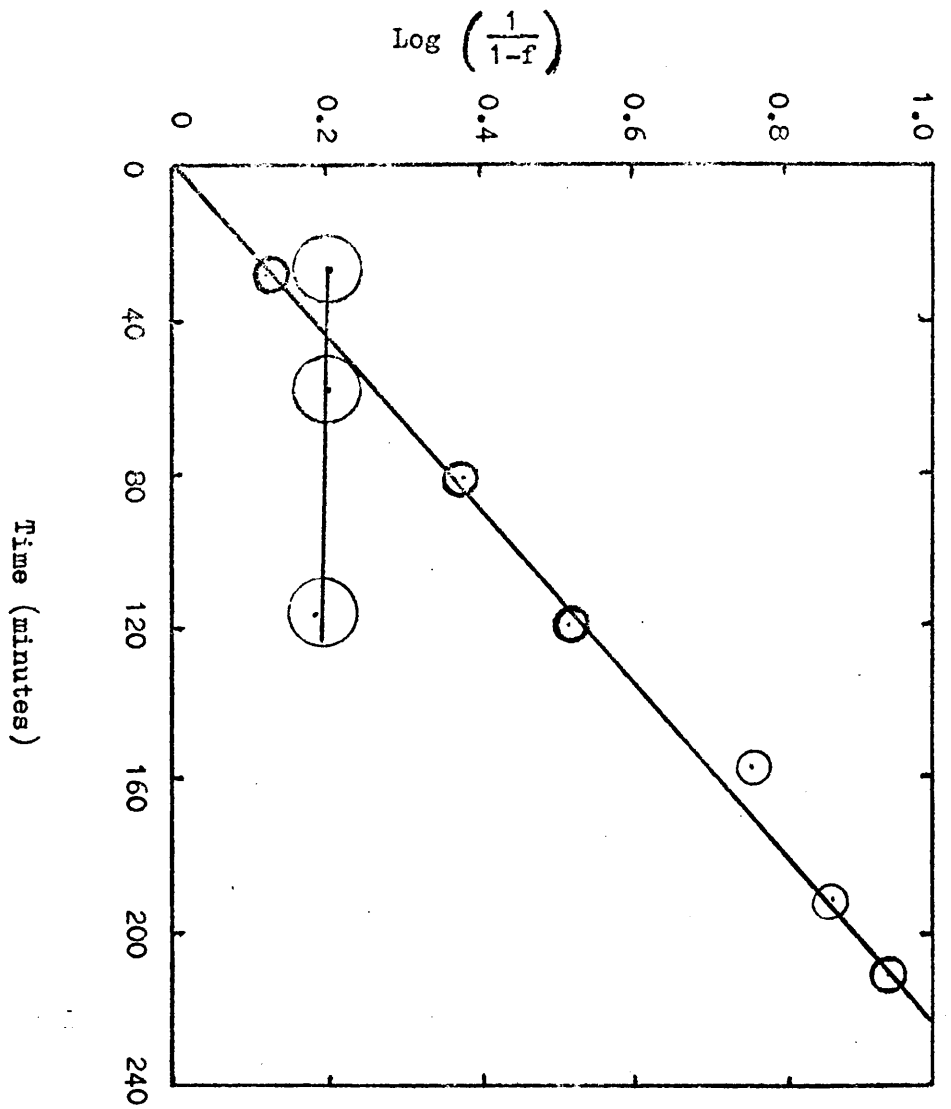
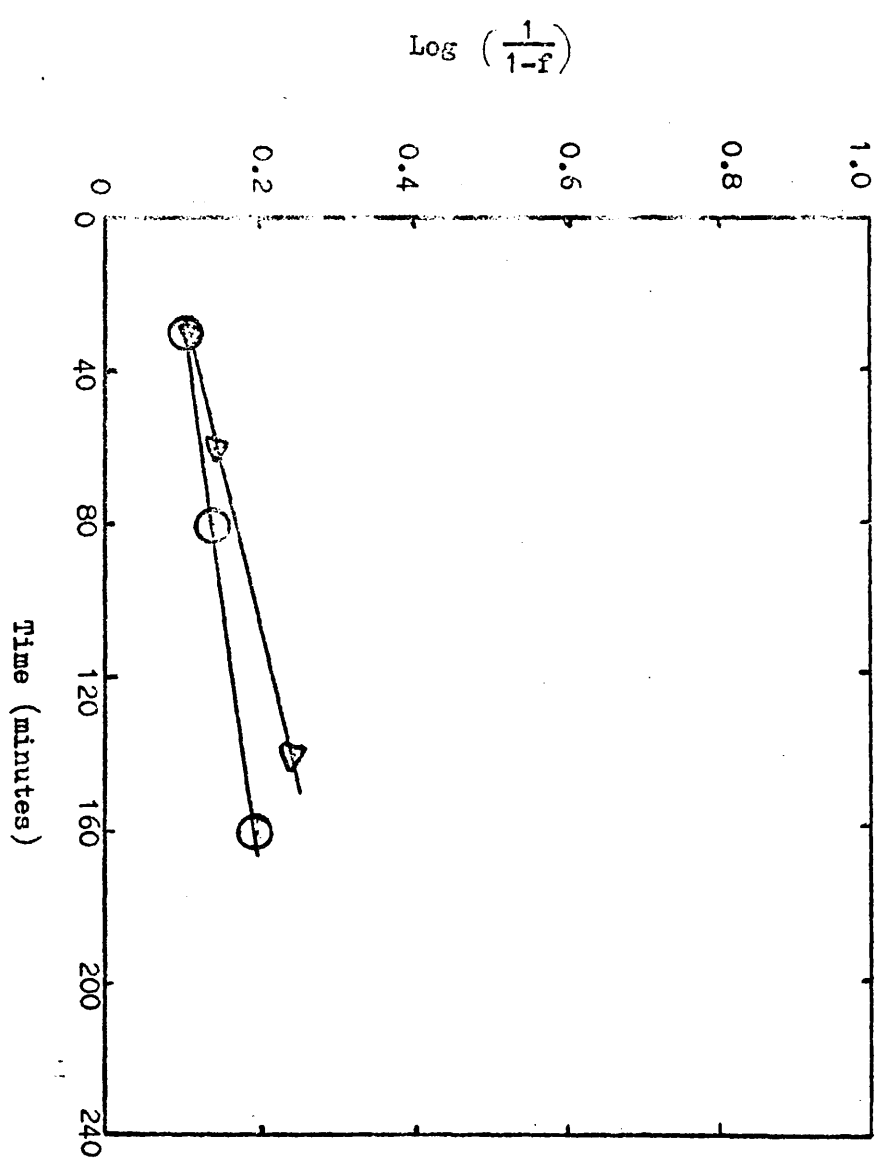


Fig. (3.1) \bigcirc WF₅OMe; \bigcirc WF₅OC₆F₅

Fig. (3.2) Plot of $\text{Log} \left(\frac{1}{1-f} \right) \underline{v}_t$ for $\text{WF}_{5\text{OPh}}$ \bigcirc and \triangle refer to two sets with different concentrations



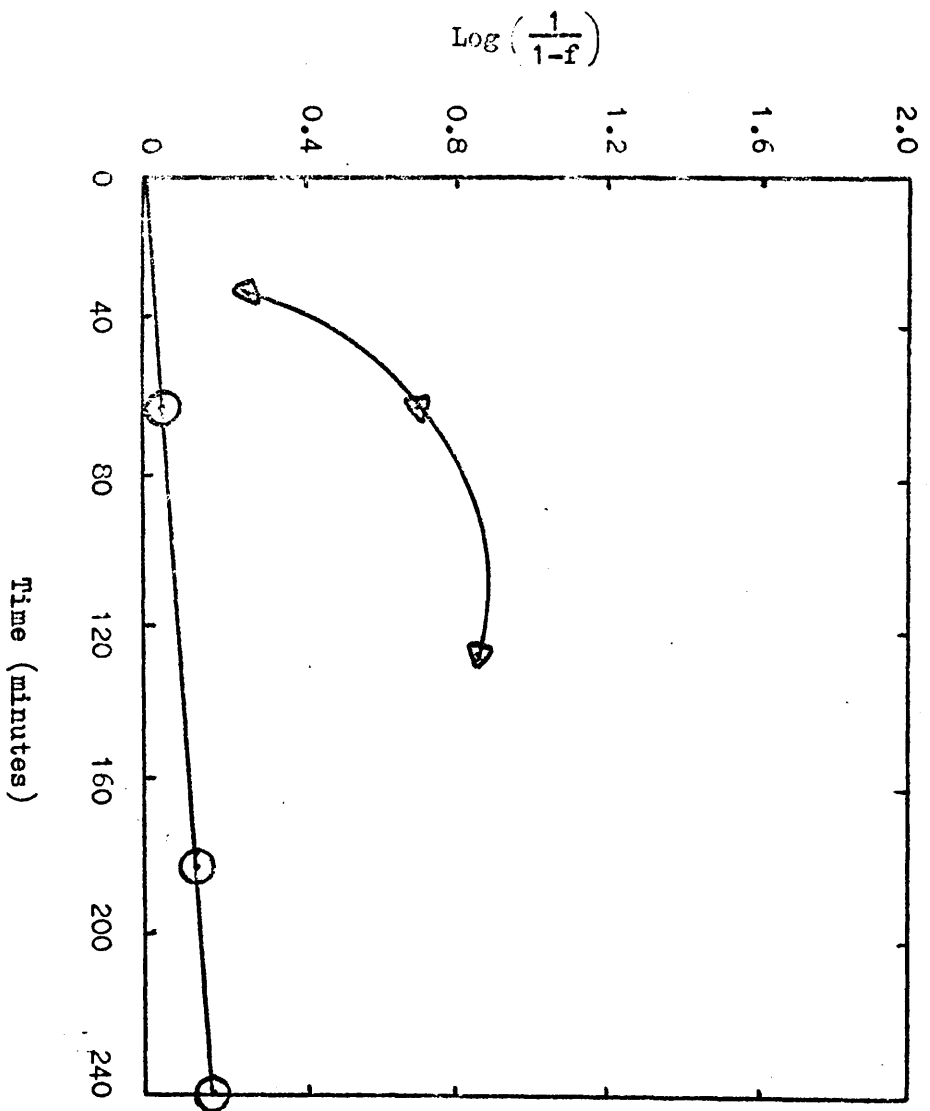


Fig. (3.3) $\Delta = WF_4(OMe)_2$ $\circ = WF_2(NEt_2)_4$

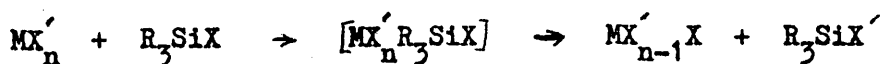
straight line passing through the origin.^{162,171} The plot of $\log\left(\frac{1}{1-f}\right)_{\text{vt}}$ for WF_5OMe (Fig. 3.1) approximates to this, which suggests almost equal rates of exchange of the two types of fluoride ligands. At this stage, the possibility of a small difference in the rates of exchange of the fluoride ligands trans to fluoride and trans to OMe cannot be completely excluded in view of the slight deviation of the plot from a straight line. The plot of $\log\left(\frac{1}{1-f}\right)_{\text{vt}}$ for $\text{WF}_2(\text{NEt}_2)_4$ is also a straight line passing through the origin which suggests that the two fluoride ligands in $\text{WF}_2(\text{NEt}_2)_4$ are kinetically equivalent. The plot of $\log\left(\frac{1}{1-f}\right)_{\text{vt}}$ for $\text{WF}_4(\text{OMe})_2$ is a curve. It is likely, therefore, that the two types of fluoride ligands exchange at different rates in this molecule. The plots of $\log\left(\frac{1}{1-f}\right)_{\text{vt}}$ for WF_5OPh and $\text{WF}_5\text{OC}_6\text{F}_5$ are straight lines which do not pass through the origin. By comparison with the gradient of the plot for WF_5OMe , the rate of exchange is apparently slow for WF_5OPh and negligible for $\text{WF}_5\text{OC}_6\text{F}_5$. It is difficult to account for the positive fraction exchange at $t = 0$ as indicated by the non zero intercepts for these compounds. It could be due to some secondary reaction such as slight hydrolysis, or to very fast initial exchange by one type of fluoride ligand. The former possibility seems most unlikely, since no secondary reaction is observed. As stated above, the observations made for $\text{WF}_2(\text{NEt}_2)_4$, $\text{WF}_4(\text{OMe})_2$, WF_5OPh and $\text{WF}_5\text{OC}_6\text{F}_5$ are based on three results in each case, and more experiments are required to verify these observations.

As described in the introduction to this chapter, exchange reactions occur via one of the three mechanisms;¹⁴² either through electron transfer between the two oxidation states of the same element (as $\text{Fe}^{2+} + \text{Fe}^{3+}$), or by the formation of a transition state through a dissociation mechanism (as $\text{IF}_7 \rightarrow \text{IF}_5 + \text{F}_2$); or by the formation of a transition state via an

associative mechanism (as $\text{UF}_6 + 2\text{NaF} \rightarrow \text{Na}_2\text{UF}_8$). In this work, the first possibility is most unlikely as the exchanging atoms (F) are in the same oxidation state in both Me_3SiF and the tungsten compounds. Since no evidence for the dissociation of the tungsten compounds used in this work has been obtained, exchange reactions via the associative mechanism are the most probable. Recently a donor-acceptor complex, $\text{Me}_3\text{SiF} \rightarrow \text{SbF}_5$ has been reported.¹⁷³ Seven co-ordinate tungsten compounds, e.g. tungsten hexafluoride-trimethylphosphine,⁴¹ have been reported. A co-ordination number higher than six is also believed to occur in the complex heptafluorotungstate, KWF_7 .⁵⁰ Thus the formation of a seven co-ordinate $\text{MF}_{6-n}\text{X}_n - \text{Me}_3\text{SiF}$ intermediate is not unlikely.

Steric hindrance in a seven co-ordinate ($\text{WF}_2\text{X}_4 \cdot \text{Me}_3\text{SiF}$) intermediate is expected to be greater the larger the substituent X. The lack of reactivity of $\text{WF}_2(\text{OMe})_4$ is therefore surprising in view of the easily measurable exchange observed for $\text{WF}_2(\text{NEt}_2)_4$. It is possible that steric factors are less significant in the formation of the intermediate than electronic considerations. Thus, the greater charge on the tungsten atom in $\text{WF}_2(\text{NEt}_2)_4$ compared with $\text{WF}_2(\text{OMe})_4$ would favour the formation of a $\text{W} \rightarrow \text{F}$ bond in the intermediate in the former case.

The mechanisms of exchange reactions are usually similar to those of the comparable substitution reactions.¹⁴² Indeed, as discussed in chapter one, the substitution reactions of Me_3SiX ($\text{X} = \text{CN}, \text{Cl}, \text{NR}_2$) with the covalent halides MX'_n ($\text{M} = \text{Ti}; \text{X}' = \text{Cl}$ and $\text{Br}; n = 4; \text{M} = \text{B}; \text{X}' = \text{F}, n = 3; \text{M} = \text{W}; \text{X}' = \text{F}; n = 6$) are believed to involve the formation of a Lewis acid-Lewis base intermediate complex.



The rates of the exchange reactions studied are therefore expected to be, in part, a measure of the chemical reactivity of the tungsten compounds towards substitution of the fluoride ligands. It should be interesting to compare their behaviour with WF_6 itself, but this exchange could not be studied due to the difficulties of separating WF_6 and Me_3SiF .

To obtain further insight into the mechanisms of the tungsten(VI) fluorides - Me_3SiX reactions, it is necessary to determine rates of exchange under identical conditions of concentration and temperature, using the techniques developed in this work. Further investigations are being carried out in this department to determine such quantitative kinetic data.

CONCLUSIONS

WF_5X ($X = NEt_2, OMe, OPh, OC_6F_5$), $cis-WF_4(OMe)_2$, and $WF_2(NEt_2)_4$ undergo ^{18}F exchange with labelled Me_3Si^*F at $22 \pm 3^\circ C$. No exchange occurs for $Me_3Si^{18}F - WF_2(OMe)_4$ at $22 \pm 3^\circ$ even after 180 minutes.

Exchange under heterogeneous conditions depends on the surface area of the compound. Under homogeneous conditions, both the concentrations of the solutions and the stoichiometry of the reactants affect the rate of exchange. A qualitative comparison of the ^{18}F exchange rate between Me_3Si^*F and substituted tungsten(VI) fluorides shows that the exchange rate also depends on the nature and number of substituents. ^{18}F exchange for $WF_4(OMe)_2$, WF_5OMe and WF_5NEt_2 is fast and nearly complete after 180 minutes. Exchange is rapid but incomplete for $WF_5OC_6F_5$. For WF_5OPh the exchange is easily measurable but apparently slow and incomplete. The rate of ^{18}F exchange for $WF_2(NEt_2)_4$ is intermediate between the fast and slow rates.

The mechanism of ^{18}F exchange reactions between Me_3Si^*F and the substituted tungsten(VI) fluorides is thought to be comparable with the reported mechanism of the substitution reactions of tungsten hexafluoride with R_3SiX ($R = Me$ or Et ; $X = NR_2, OMe, OPh, OC_6F_5, CN, NCO$ etc.). In both cases, a seven co-ordinate donor-acceptor intermediate is postulated.

Further quantitative kinetic studies of the exchange reactions, under similar conditions of temperature and concentration, are required to determine the rates of these reactions, which can be used for comparison of the chemical reactivities of tungsten compounds.

EXPERIMENTAL

Standard vacuum techniques were used. Me_3SiF was obtained either as a by-product from the reaction of WF_6 with Me_3SiX ($\text{X} = \text{NEt}_2$, OMe , OPh), or, in some cases, from the reaction of WF_6 with a six-fold excess of Me_3SiCl maintained at 20° for 3 weeks.⁵⁰ The purity of Me_3SiF was confirmed by comparing its i.r. and n.m.r. spectra with those reported,^{95,169} and by molecular weight determination. (Molecular weight found ranged between 91.5 - 93.8; Me_3SiF requires 92.0). A small amount of the sample of Me_3SiF obtained from the reactions of WF_6 with Me_3SiCl was distilled under vacuum on to an aqueous solution of AgNO_3 , but no turbidity was observed, indicating that Me_3SiCl was not present as an impurity. The purification of WF_6 and C_6F_6 and the preparation of WF_5NEt_2 , $\text{WF}_5\text{OC}_6\text{F}_5$ and $\text{WF}_2(\text{NEt}_2)_4$ have already been described (chapters one and two). WF_5OPh and $\text{WF}_{6-n}(\text{OMe})_n$ ($n = 1, 2$ and 4) were prepared from the stoichiometric reactions of WF_6 with Me_3SiX ($\text{X} = \text{OPh}$, OMe). Their ^{19}F and ^1H n.m.r. spectra were found to be identical with those reported.⁸⁷

Radioactivity Measurements

^{18}F activity was determined using a NaI well scintillation counter (Ekco instruments, Scaler-Timer M 5024B and Ratemeter M 5050B) with well dimensions $\left(\frac{25}{16}\right)'' \times \left(\frac{25}{32}\right)''$ diameter. Samples were contained in pyrex ampoules of uniform bore (10 mm dia.; 5 ml. volume) and fitted with P.T.F.E.-glass stopcocks (Fischer and Porter). Me_3SiF and WF_6 were counted in the liquid phase. In the preliminary experiments, pure tungsten compounds were counted, but it was then found that counting efficiency largely depended on the geometry of the system.

Thus, maximum efficiency was observed when the sample was at the bottom of the flask. However, counting efficiency was improved when the sample was either a liquid or in solution. Reproducible results were obtained when the samples were counted in solutions of C_6F_6 or acetone.

Preparation of Labelled Me_3SiF

Fluorine-18 was prepared by neutron irradiation of lithium carbonate (2 gm. B.D.H. AnalaR) for one hour at a flux of $3 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ according to ${}^6\text{Li}(n, \alpha)t$; ${}^{16}\text{O}(t, n){}^{18}\text{F}$. The irradiation was carried out in the Scottish Universities Research Reactor, East Kilbride. Active Li^{18}F was dissolved in 50% H_2SO_4 and the solution was distilled at 100° . The H^{18}F evolved was then absorbed in a 0.15 molar solution of aqueous CsOH at 0° giving an aqueous solution of Cs^{18}F . The solution activities were typically 0.2 mCi. Neutralization with 40% HF followed by evaporation and drying (1 hour; i.r. lamp) gave solid Cs^{18}F which was further dried in vacuo.¹⁵⁹

Me_3SiF was labelled by exchange with Cs^{18}F in a stainless steel (75 ml.) pressure vessel (Hoke Ltd.) fitted with a Hoke needle valve. It was kept at $50-60^\circ$ for 45-60 minutes. The radiochemical purity of Me_3SiF was checked by a decay curve determination over at least three half-lives. Calculated half-lives agreed with the previously reported value of 112 minutes.¹⁵⁶ A typical decay curve is shown in Fig. (3.4). The half-life of ${}^{18}\text{F}$ calculated from the slope of the graph, which is equal to $\frac{0.301}{t_{1/2}}$,¹⁴² is 111.2 minutes.

Exchange Reactions

The experimental procedure for all the exchange reactions studied was

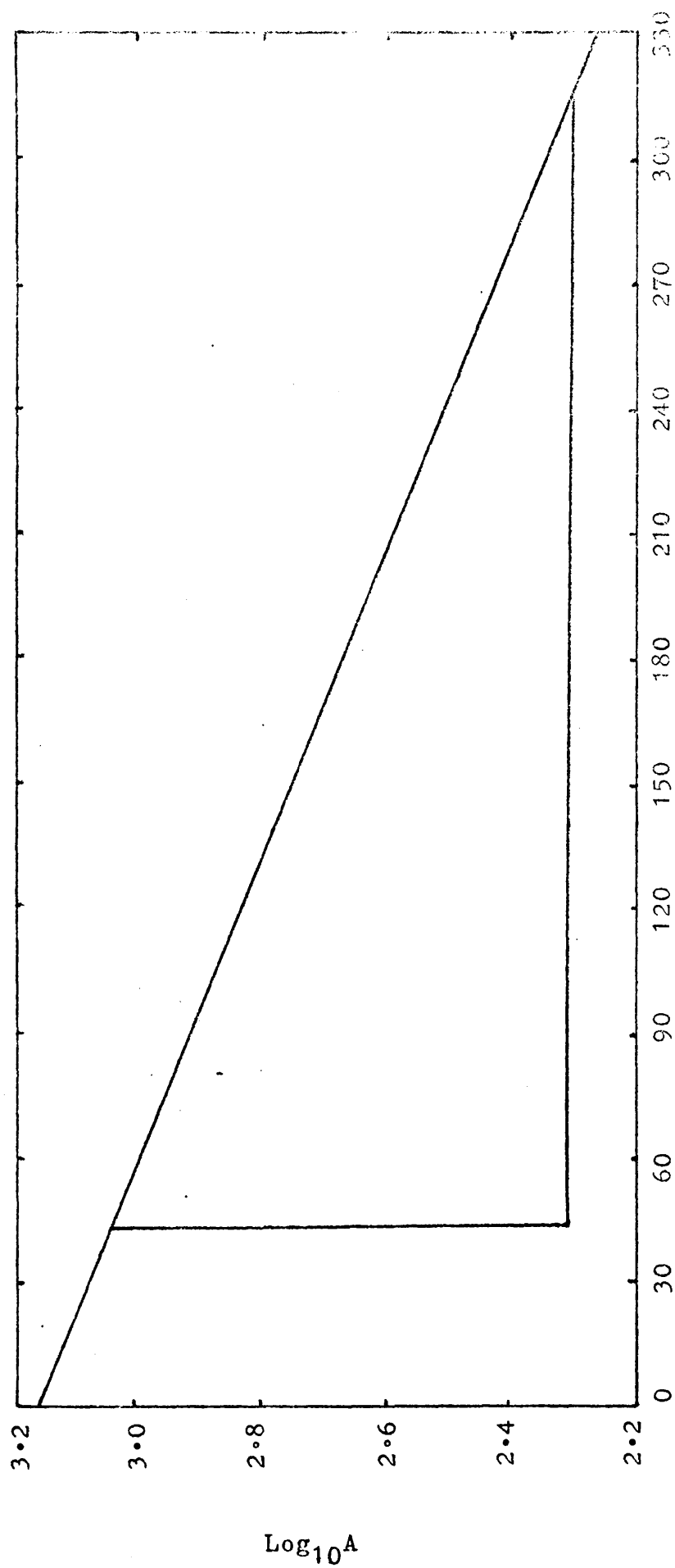


Fig. (3.4) Decay curve of ^{18}F

the same. A known weight of the labelled Me_3SiF , whose specific activity had been determined, was distilled directly on to a known weight of unlabelled tungsten compound, in a pyrex ampoule (volume 5 ml. bore 10 mm.). For the exchange reactions in homogeneous systems, solutions of known concentration, determined by weights, of tungsten compounds in C_6F_6 were used. All exchange reactions were carried out at $22.0 \pm 3^\circ$ for varying lengths of time (15 minutes - 240 minutes). After the exchange, the volatile fraction ($\text{Me}_3\text{SiF} + \text{C}_6\text{F}_6$) was removed at -60° , and the activities of both fractions were determined and corrected for ^{18}F decay. In all cases the radiochemical balance was within 95% and there was no evidence of hydrolysis or other chemical reactions. The radiochemical purity of all new species labelled was checked by decay curve determination over at least two half lives. Calculated $t_{1/2}$ values agreed with the reported value of 112 minutes.¹⁵⁶ To ensure the complete separation of ($\text{Me}_3\text{SiF} + \text{C}_6\text{F}_6$) from the tungsten compound, the weight of the two fractions were compared with the original weights of the reactants, and were found to be identical. Separate samples of the tungsten compound were prepared and used for each determination.

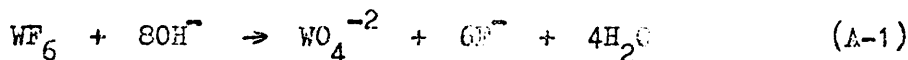
In the preliminary experiments, no exchange was observed between inactive C_6F_6 and the labelled Me_3SiF or labelled tungsten compound, and between C_6F_6 and labelled CsF at temperatures up to 350° . The exchange between WF_6 and active CsF was very rapid at $22 \pm 3^\circ\text{C}$, but, due to the difficulty of separating Me_3SiF from WF_6 , the exchange between WF_6 and labelled Me_3SiF could not be studied. The separation of Me_3SiF from WF_6 was attempted both by physical means (distillation) and by chemical means. The separation by distillation was attempted at -100° and -80°C

At -100° the separation was very slow and thus could not be used for the exchange reactions of short duration (30 minutes - 240 minutes). At -80° , some WF_6 also distilled with Me_3SiF . The chemical methods investigated were the hydrolysis of WF_6 by NaOH and complex formation of WF_6 with C_6F_6 or pyridine. In both cases, Me_3SiF was also found to react (evidence from the infra-red of the volatile fraction distilled from the reaction mixture), though the nature of the reaction was not investigated.

APPENDIX ONE

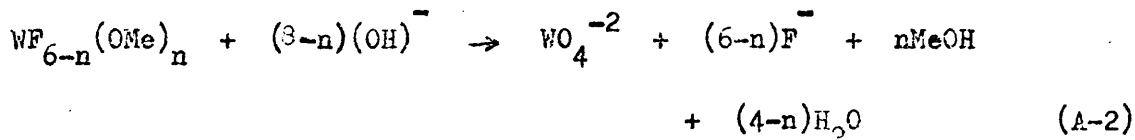
HEATS OF FORMATION OF METHOXY TUNGSTEN(VI) FLUORIDES

Tungsten hexafluoride hydrolyses according to the reaction.¹⁷⁴



Since heats of formation of $\text{WO}_4^{2-}(\text{aq.})$, $\text{F}^-(\text{aq.})$, $\text{OH}^-(\text{aq.})$ and H_2O (liquid) are all known,¹⁷⁵ the heat of hydrolysis of WF_6 can be used to calculate its heat of formation.¹⁷⁴

It seems reasonable to assume that methoxy tungsten(VI) fluorides hydrolyse according to similar reaction schemes. The appropriate reaction can be represented as follows :



As heats of formation of all the species in equation (A-2) are known¹⁷⁵ (Table A-2), the heats of hydrolysis of the reaction (A-2), by analogy with WF_6 , can lead to the heats of formation of methoxy tungsten(VI) fluorides.

Heats of hydrolysis of methoxy tungsten(VI) fluorides, $\text{WF}_{6-n}(\text{OMe})_n$ ($n = 1, 2$ and 4) have been determined by Professor R.D. Peacock and Dr. J. Burgess at the University of Leicester,¹⁷⁶ using the samples of tungsten compounds prepared in this work. The results are given in Table (A-1).

Heats of formation of methoxy tungsten(VI) fluorides were calculated from the expression (A-3) derived from (A-2).

$$\Delta H_f^\circ \text{WF}_{(6-n)}(\text{OMe})_n(\text{aq.}) = \left[\Delta H_f^\circ (\text{WO}_4^{2-})(\text{aq.}) + (6-n)\Delta H_f^\circ \text{F}^-(\text{aq.}) + n\Delta H_f^\circ (\text{MeOH})(\text{aq.}) + (4-n)\Delta H_f^\circ (\text{H}_2\text{O}) \right] - \left[(3-n)\Delta H_f^\circ (\text{OH})^-(\text{aq.}) + \text{heat of reaction (A-2)} \right]. \quad (\text{A-3}).$$

Table (A-1)

Heats of Hydrolysis of Methoxy Tungsten(VI) Fluorides

Compound	Heats of Hydrolysis Kcal.mol ⁻¹
WF ₅ OMe	-105.9 ± 3.6
WF ₄ (OMe) ₂	- 89.8 ± 2.0
WF ₂ (OMe) ₄	- 61.5 ± 1.1

Table (A-2)

Heats of Formation of Some Compounds in Equation (A-2)

Compound	Heats of Formation Kcal.mol ⁻¹	Ref.
WO ₄ ⁻² (aq)	-257.1	175
OH ⁻ (aq)	- 55.0	175
H ₂ O(l)	- 68.3	175
F ⁻ (aq)	- 79.5	175
MeOH(aq)	- 58.8	175

Table (A-3)

Heats of Formation of Methoxy Tungsten(VI) Fluorides and Tungsten Hexafluoride

Compound	Heats of Formation
	Kcal.mol ⁻¹
WF ₆	-422 174
WF ₅ OMe	-427
WF ₄ (OMe) ₂	-402
WF ₂ (OMe) ₄	-370

APPENDIX TWO

Apparatus and Instrumentation

Standard vacuum line techniques were used throughout and rigorous precautions were taken to exclude moisture from all systems. In particular, all glassware was flamed out before each experiment. A vacuum line system was constructed from a pyrex glass manifold (30 mm bore), which could be evacuated by a three-stage mercury diffusion pump backed by an Edwards two-stage rotary pump. Standard ground glass joints and Teflon glass stop-cocks (Fisher Porter Co.; ACE glass Inc.; Quickfit "Rotaflo") were used where required. The joints were lubricated either with Apiezon 'N' grease or, where necessary, the polyfluorochlorocarbon, Kel-F90 (B.D.H., K.W. Chemicals or Gallenkamp). In some cases, joints were waxed with Kel-F90 polymer wax (3M).

In view of the many operations carried out by vacuum techniques, the separation of mixtures of volatile compounds, the determination of molecular weight by the vapour density methods, the preparation of gas samples for i.r. spectroscopy and liquid samples for n.m.r. spectroscopy, it was necessary to compromise between a joint free system and one which could be easily dismantled for cleaning. However, a ~~pressure~~ of less than 10^{-4} mm. mercury was always obtained. (The vacuum was monitored either by an Edwards vacustat, or by, the colour of the discharge from a H.F. Tester coil (Edwards High Vacuum Ltd.).)

Involatile compounds were handled in a Lintott inert atmosphere box. Oxygen-free nitrogen was circulated over activated molecular sieves, and the water level in the box was monitored using an Elliot moisture monitor (model 111), fitted with a P_2O_5 electrolytic cell. The water level in the

box was below 14 p.p.m., when it was used for transfer of hygroscopic materials. Readings from the monitor, when the inert atmosphere box was dried with dishes of P_2O_5 , suggested that the water level in a conventional dry box is between 80 and 300 p.p.m.⁷⁸

Reaction vessels were pyrex-glass (volume ca. 25 ml.) and were fitted with PTFE-stopcocks. For ^{18}F tracer work, the pyrex-glass reaction vessel used was of uniform bore (10 mm. dia., 5 ml. volume). The two types of reaction vessels are shown in Figs. 1 and 4 respectively.

Molecular weights of $WF_2(NEt_2)_4$, WF_5OMe and $WF_5OC_6F_5$ were determined under vacuum by vapour pressure measurements on solutions of tungsten compounds in C_6F_6 . The apparatus used for this purpose was designed for this work and is shown in Fig. (5).

Densities were determined from measurements in vacuo using a dilatometer calibrated with mercury. Times of viscous flow were measured using an Oswald viscometer adapted for vacuum use.¹⁷⁷ (Fig. 2). Measurements were made on two separately prepared samples in a thermostated bath, which could be controlled to $\pm 0.5^\circ C$ over a range of temperature.

Conductometric titrations were carried out by means of a Wayne Kerr conductivity bridge; model B. 221. The cell used for conductometric titrations was specially adapted for vacuum use (Fig. 3). The detailed procedure is given in chapter one.

Infra-red spectra of gases were taken in 5 cms. gas cells with KBr windows, and pressures were measured with a mercury manometer. Solid samples were obtained as Nujol or fluorolube mulls using AgCl, KBr or CsI plates, as appropriate. Liquid samples were obtained neat by pressing a drop between KBr or AgCl plates. The following instruments were used:- Perkin-Elmer, 237, 257, 337 and 457 in their appropriate ranges.

The Raman spectrum was run on a Cary 81 Raman spectrometer (University of Strathclyde) fitted with a Spectra Physics 125 Helium-Neon Laser source with excitation at 6328\AA° .

N.M.R. spectra were obtained using a Perkin-Elmer R-10 or Jeol C.60 HL spectrometer operating at 60.0 MHz. for ^1H and 56.46 MHz. for ^{19}F , with a probe temperature of 33.5° . Volatile samples were distilled into pyrex tubes sealed to the vacuum line. Involatile samples were also prepared under vacuum by tipping a portion into an n.m.r. tube attached to a glass vessel (Fig. 1). Solvents and internal references were distilled into the n.m.r. tubes under vacuum. Fluorine spectra were measured in p.p.m. relative to trichlorofluoromethane, CCl_3F , and proton spectra were referenced with tetramethylsilane (T.M.S.), Me_4Si . ^1H chemical shifts (p.p.m.) given in this thesis are all at low field of TMS except where mentioned. ^{19}F chemical shifts at low field to CCl_3F are given negative values while those up-field to CCl_3F (all in p.p.m.) are given positive values.

Mass spectra were recorded at 70 eV. using an AEI. MS 12 spectrometer.

Ultraviolet spectra were recorded on a Pye Unicam SP 800B spectrophotometer.

Elemental analysis Tungsten was determined gravimetrically as WO_3 , using cinchonine hydrochloride to facilitate precipitation. Analysis for other elements were performed by Beller (Göttingen, W. Germany) or Bernhardt (W. Germany).

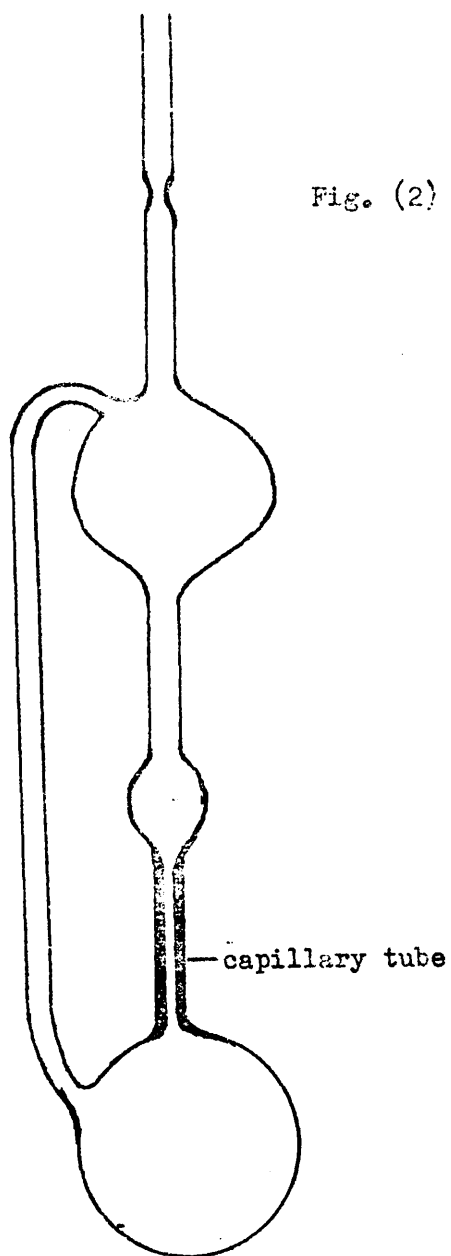


Fig. (2) Viscometer

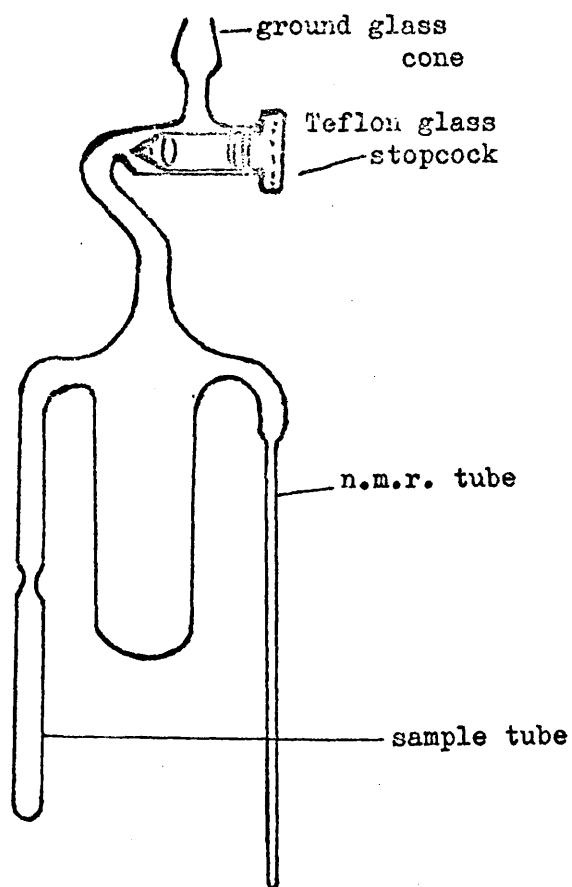


Fig. (1) Reaction Flask

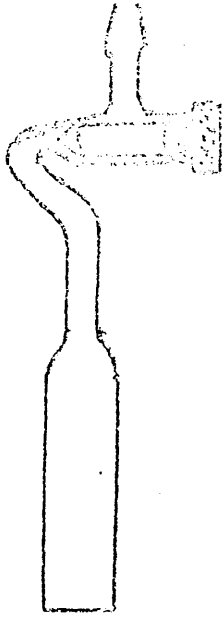


Fig. (4) Flask used in
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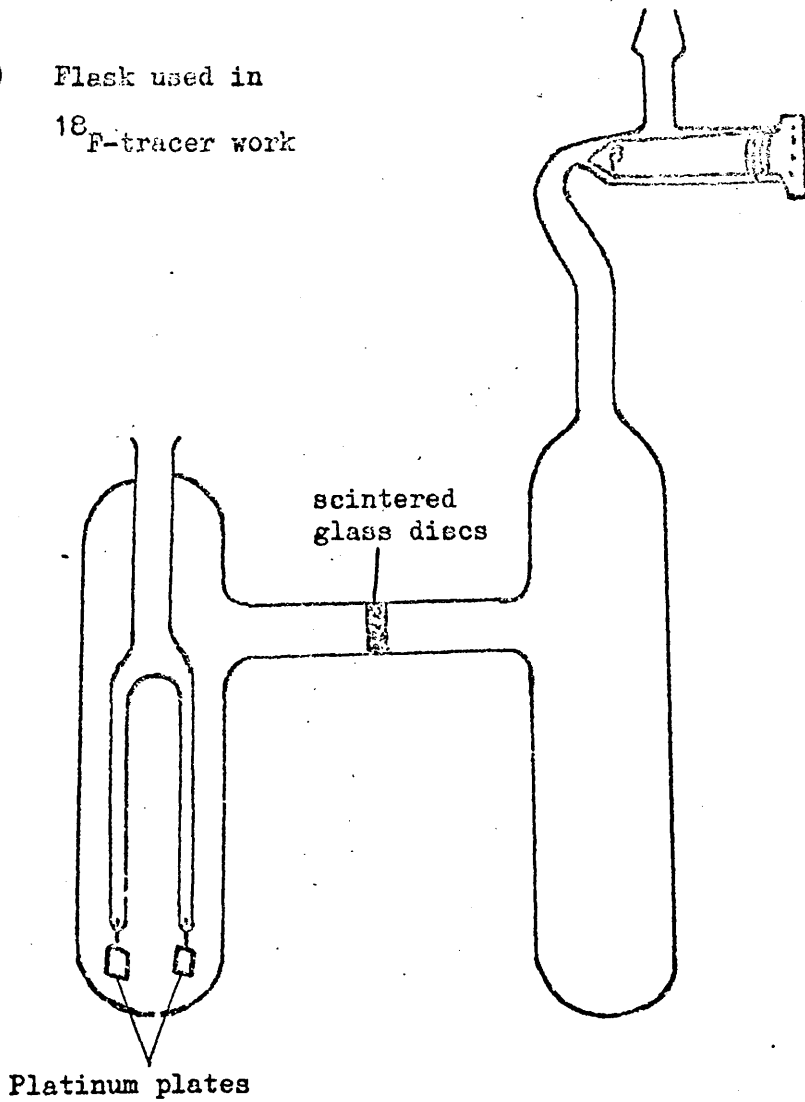


Fig. (3) Conductivity Cell

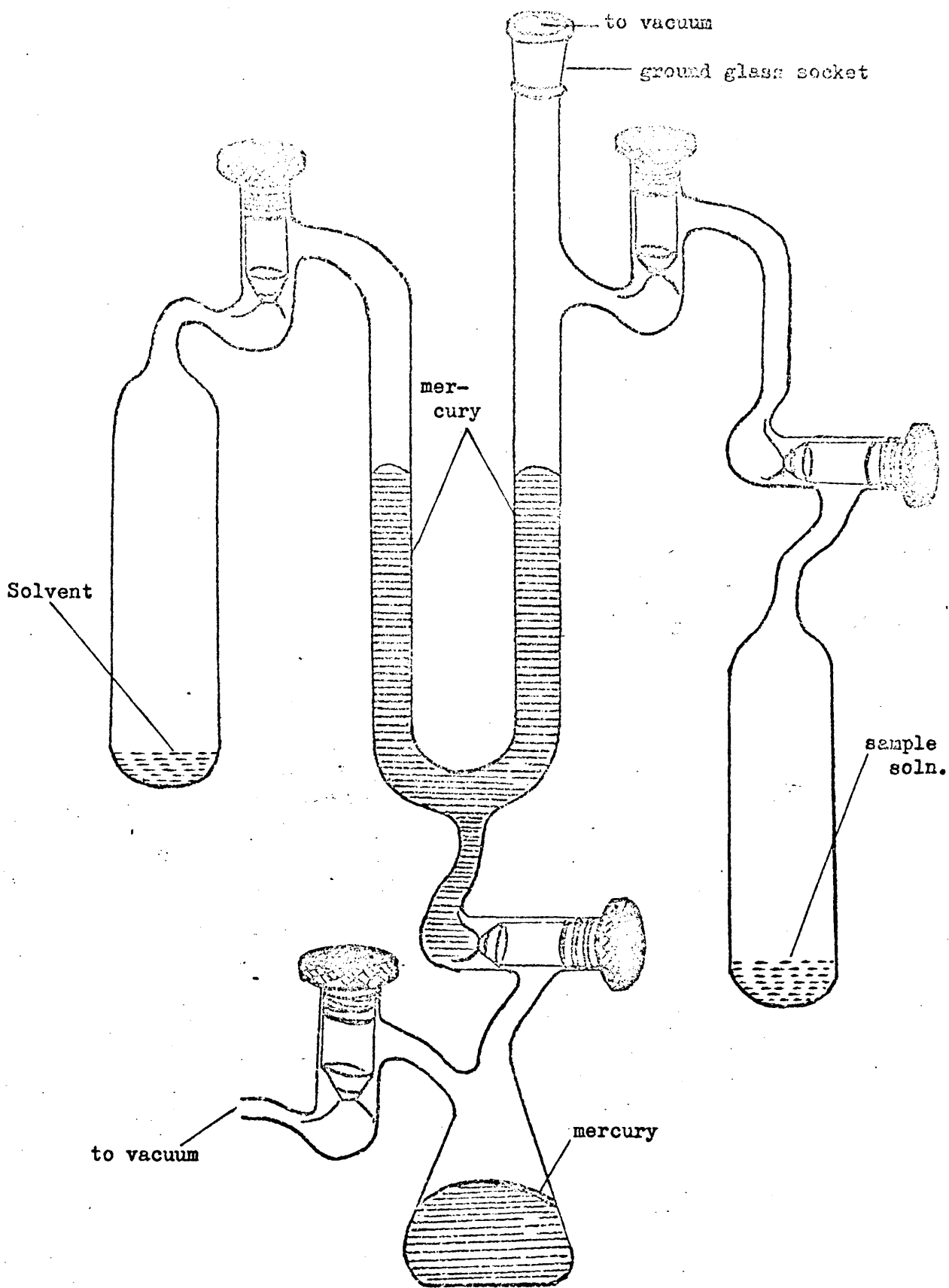


Fig. (5) Molecular Weight Apparatus

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